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The Journal
of the
Society of Dyers and Colourists

Volume 74 Number 3

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THE SOCIETY OF DYERS AND COLOURISTS
DEAN HOUSE PICCADILLY BRADFORD YORKSHIRE

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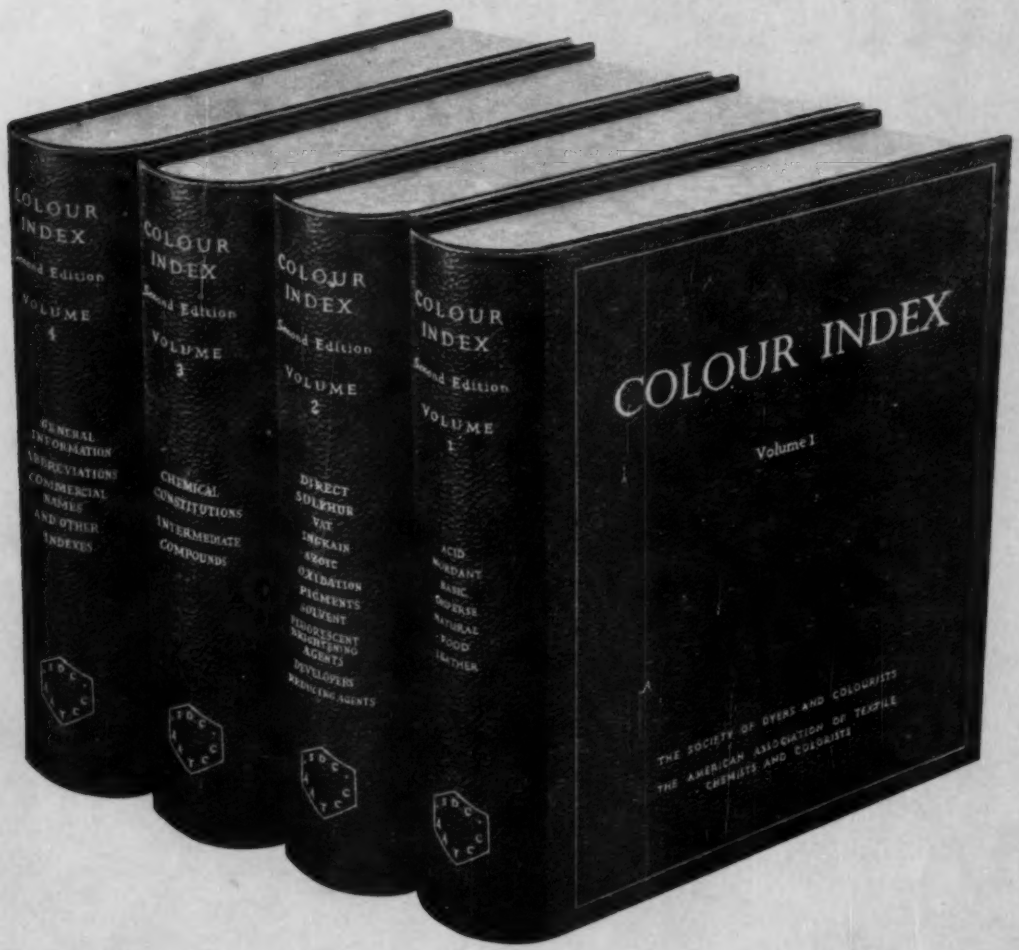

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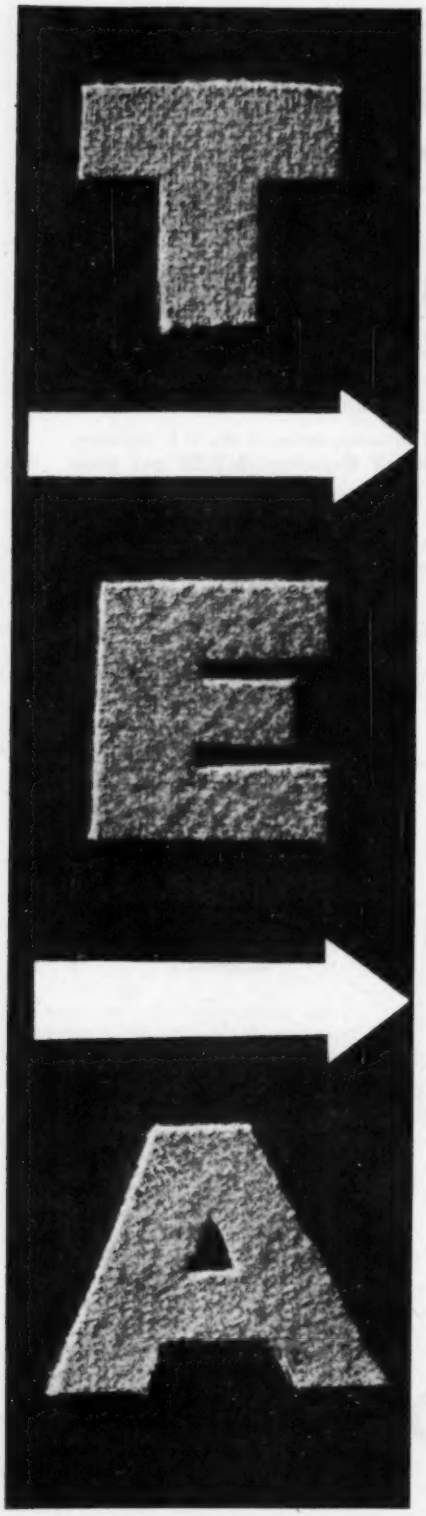

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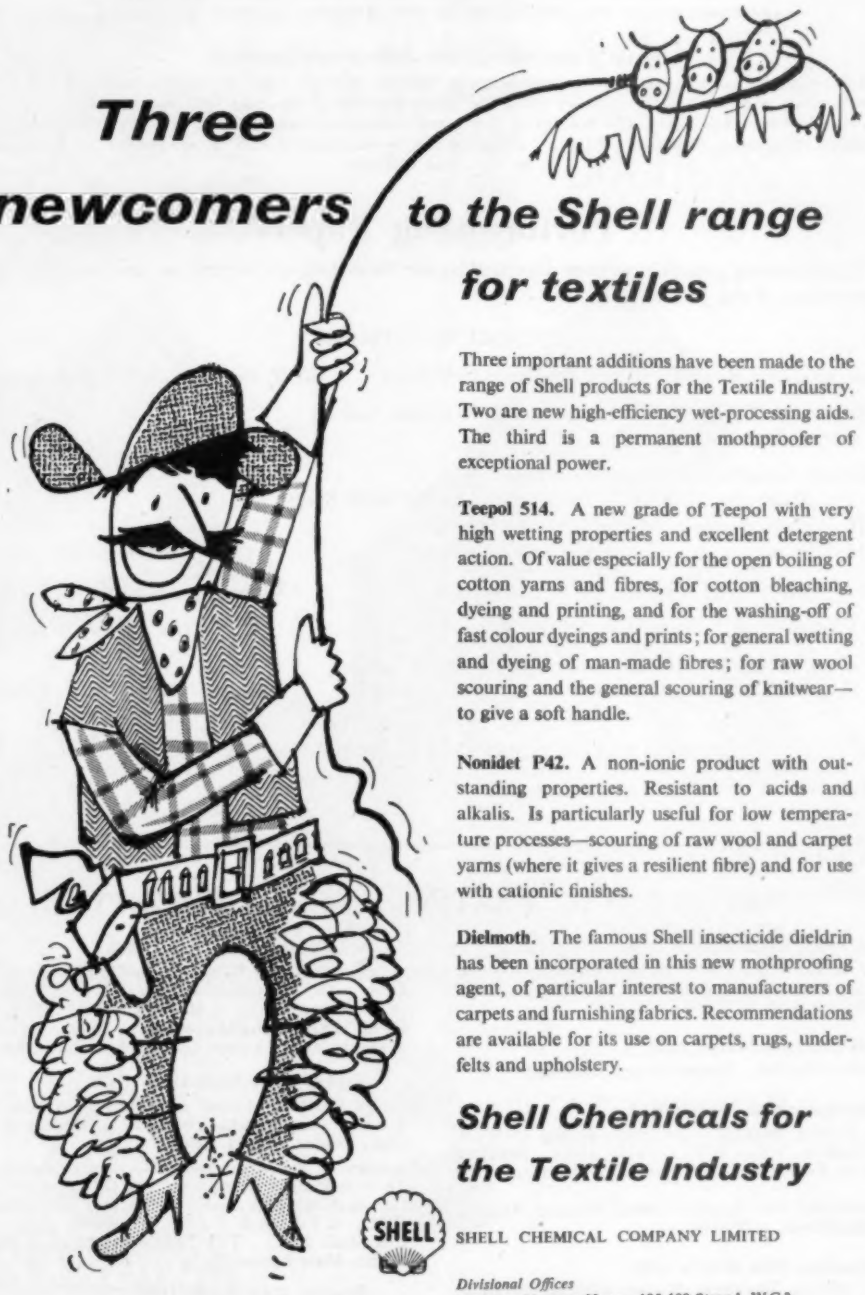

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–7 of the January 1958 and pages 285–290 of the July 1957 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

COMMUNICATIONS

Adsorption of a Reactive Dye by Modified Celluloses — *E. H. Daruwalla and P. Subramaniam*

Studies in the Transfer of Disperse Dyes to Cellulose Acetate during Steaming — *E. H. Daruwalla and V. R. Limaye*

Studies in Aminoanthraquinone Compounds
I— Absorption Spectra in Solution and in the Solid State
II— Photochemistry of Dyed Polymer Films
III— Photochemistry in the Solid State — *G. S. Egerton and A. G. Roach*

Dyeing Properties of Mature and Immature Cotton — *Nils-Bertil Furvik*

The Chemistry of Esters of Leuco Vat Dyes— III — *A. Johnson and M. L. Rahman*

The Determination and Significance of Crystallite Size in Regenerated Cellulose Fibres — *D. N. Tyler and N. S. Wooding*

EXPLANATORY PAPER ON MODERN THEORY

Surface Activity, Solution, and Adsorption — *C. H. Giles*

FORTHCOMING MEETINGS OF THE SOCIETY

Saturday, 22nd March 1958

NORTHERN IRELAND SECTION. Annual General Meeting and Dinner. Thompson's Restaurant, **Belfast.** A.G.M. 5 p.m. Dinner 6.30 for 7 p.m.

Tuesday, 25th March 1958

HUDDERSFIELD SECTION. Annual General Meeting.

Thursday, 27th March 1958

BRADFORD JUNIOR BRANCH. *Continuous Dyeing of Wool.* D. R. Lemin, Esq., B.Sc. (I.C.I. Ltd.). Bradford Institute of Technology, **Bradford.** 7.15 p.m.

WEST RIDING SECTION. Annual General Meeting. Victoria Hotel, **Bradford.** 7.30 p.m.

Saturday, 29th March 1958

BRADFORD JUNIOR BRANCH. Annual General Meeting. Bradford Institute of Technology, **Bradford.** 10.15 a.m.

Thursday, 3rd April 1958

MIDLANDS SECTION. *Recent Trends in Dyeing for the Carpet and Hosiery Trades.* W. Beal, Esq., B.Sc. (Geigy Co. Ltd.). Messrs. Carpet Trades Ltd. Canteen, Mill Street, **Kidderminster.** 7.30 p.m.
(Joint with the Textile Institute, Kidderminster Section.)

Wednesday, 16th April 1958

MIDLANDS SECTION. *Basic Principles of Dyeing with Disperse Dyes.* D. Finlayson, Esq., M.C., M.A., D.Sc. and H. C. Olpin, Esq., M.Sc., F.R.I.C., F.S.D.C. King's Head Hotel, **Loughborough.** 7 p.m. (Preceded at 6.30 p.m. by the Annual General Meeting of the Section.)

Friday, 18th April 1958

LONDON SECTION. *Colour Fastness Requirements of Luton Textiles.* I. Glasman, Esq., A.T.I. (Marks & Spencer Ltd.). George Hotel, **Luton.** 7 p.m.

MANCHESTER SECTION. Annual General Meeting. 7 p.m. To be followed by a paper entitled *Bleaching of Cotton and Cotton Blends with Hydrogen Peroxide.* L. Chesner, Esq., B.Sc., A.T.I. and G. C. Woodford, Esq. (Laporte Chemicals Ltd.). The Textile Institute, 10 Blackfriars Street, **Manchester 3.**

Friday, 25th April 1958

The Society's Annual General Meeting and Dinner. The Central Hotel, **Glasgow C.1.**

Friday, 2nd May 1958

LONDON SECTION. Annual General Meeting and Dinner. Aldwych Brasserie, Aldwych, **London, W.C.2.** 6 p.m. for 6.30 p.m. (Mr. C. O. Clark will speak on the standards required for the A.S.D.C. examination.)

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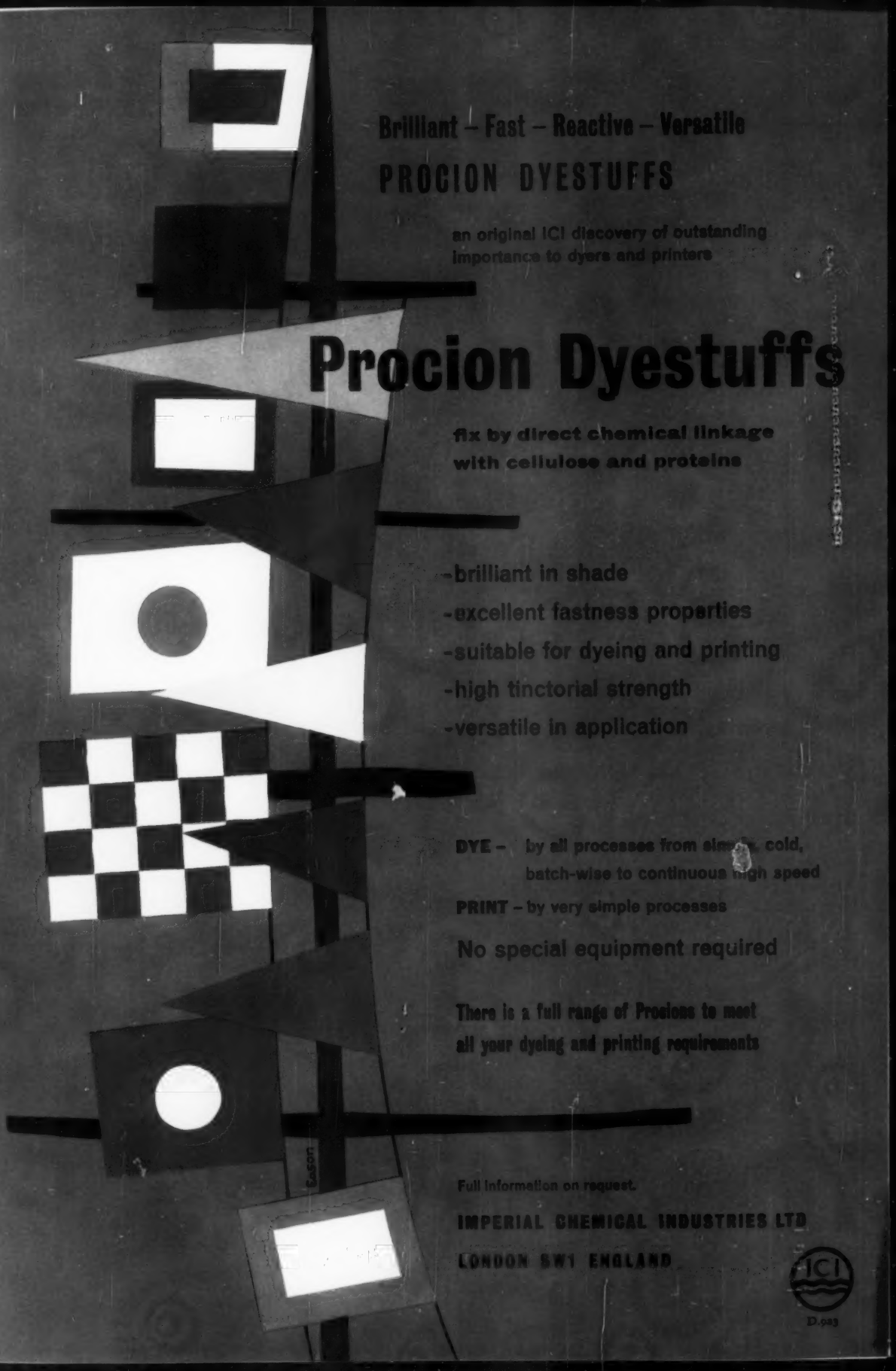
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Volume 74 Number 3 MARCH 1958 *Issued Monthly*

Proceedings of the Society

Symposium on "Recent Advances in the Colouring of Man-made Fibres"

The Society held its eighth Symposium, on *Recent Advances in the Colouring of Man-made Fibres*, at the Palace Hotel, Buxton, on Wednesday–Friday, 18–20th September 1957. The attendance at the technical sessions exceeded 200, including several from the Continent (including the U.S.S.R.), the U.S.A., and Japan

Opening of the Symposium

Wednesday, 18th September 1957, at 3 p.m.

The Symposium was formally opened by the President of the Society (Mr. CLIFFORD PAINE)

Mr. PAINE paid tribute to the organising committee and its chairman, Mr. R. K. Fourness, for the work that they had done in preparing the way for the Symposium. He extended a very sincere welcome to guests and visitors from overseas countries, and read a cable of greeting from the President-elect, Mr. John Boulton, who was at that time in the U.S.A.

The Opening Address, on *The Impact of Man-made Fibres upon the Dyeing Industry*, was given by Mr. A. H. Wilson, F.R.S., a Managing Director and Director of Research of Courtaulds Ltd.

The Symposium Dinner

The Symposium Dinner and Dance was held on Friday, 20th September 1957, under the presidency of Mr. Clifford Paine.

"THE SOCIETY OF DYERS AND COLOURISTS"

After the toast of "Her Majesty the Queen", that of "The Society of Dyers and Colourists" was proposed by—

Mr. DONALD KABERRY, T.D., M.P., who congratulated the President and those associated with him upon the success of the Symposium. As he looked around he saw tired and jaded members of the Society, worn out with the cares which had been thrust upon them during the last few days, being replenished by the food and the charm of the ladies surrounding them.

The Symposium was attended by representatives from many far distant places, and it was surely to the advantage of this country as a whole that the Society could attract representatives almost from round the world—the U.S.A., the U.S.S.R., Japan, Sweden, Switzerland, Holland, France, Germany, Czechoslovakia, and Lancashire. He spoke as a citizen of the leading city in the leading county, for after all Yorkshire lies to the east of Lancashire, and it was from the East that the wise men came.

His simple task was to propose the toast of good fortune and prosperity to the Society as a whole and to all members individually. He had seen, as it were from the side-walk, the activities of the dyers and colourists. A department of the University of Leeds pays quite a lot of attention to colouring, and even in his constituency the Wool Industries Research Association is particularly concerned with many of the things that the Society has to do.

The Society is not merely a collection of persons anxious to share out what is already known, but is determined to encourage enterprise in research and to seek out new fields to conquer. It is evident that the die has not been cast for ever.

Coming from the West Riding, he had seen how much the textile industries depend on dye research for more and more colour ranges. He was told that there are some 5,000 dye entities with over 25,000 commercial names. Indeed, as a non-technician and a member of the lower middle class group of this country, he envied the technical success of members of the Society.

At that time of the year it was the female in each household who drew attention to the new autumn shades for clothes or to the new muted shades in stockings, which, as far as he could judge, range from shadow grey to a light warm cocoa—as for the male, he has to exist at weekends with an old drab brown coat. He must confess to some measure of disappointment that the members of the Society were dressed in plain black and white—he had imagined that they would have worn some examples of their own delightful shades, and the idea might quickly spread. As far as his colleagues were concerned, they seemed to show colour in their ties alone. How much more attractive is John Bull with his waistcoat of the Union Jack! The Leader of the Opposition might appropriately attend Parliament in a jacket of

dusty rose, a scarlet waistcoat, and trousers of tender pink.

Members of the Society provide joy and colour in our lives, and ladies' fashions without the aid of dyers would be dull and dreary. Members might be regarded as licensed gay deceivers, and on request could certainly gild a lily. The new kind of fashion, a sack or a bag, without a line or a curve, without any colour or dye, did not favour the industry. Indeed, if sacks were sacks in fact, members would have been given the sack at once.

From the Society's formation to the present time, advance has continued as a result of members' researches. They are concerned not only with cloth printing; they also supply colour in our food. Of all precious gifts, colour is the most important. Even in skiffle times the moon remains blue.

The Society was founded at a time of scientific advance. Those were days of happy active lively people, no super travel, no television, no plastics, no nylon. Our habits and customs have advanced quickly and rapidly since 1884. The foundation of the Society coincided with the adoption of a National Health Act, a section of which referred to clothing. At that time it was very dull snuff brown. This may be because of the type of cloth which was strongly recommended to ward off colds, said to be caused by the sudden rush of cold air and not by viruses— there was no Asian 'flu.

Mr. Kaberry referred briefly to the scheme of European Free Trade, with which members of the present government are concerned. Although markets for our goods would be extended, at the same time more severe competition would be provided by our European counterparts. It is clear that some improvements of our industries must take place, and the dye industry and all allied trades will require special consideration. The suggestion is of the greatest concern to those engaged in these industries. It presents a challenge to the members of this Society to overcome these difficulties, and to show the strength of the British scientific worker. We shall gain nothing by sitting back and bemoaning the advances made by other countries. It is on the scientific capacity of the research workers of this country that our prosperity depends. Members of this Society have a great part to play in this. So, as in 1884, with the high hopes the foundation of the Society had for the future, I hope that likewise, 73 years after, each member of the Society will dedicate himself to the task of accepting the challenge at the present time to secure the fruits of scientific research.

Mr. CLIFFORD PAINE (*President of the Society*), in replying to the toast, said that it is generally supposed that the scientist and the technologist are basically ignorant of the arts and the humanities, and that they have never been exposed to a liberal education. He was left in doubt, therefore, whether it is basic ignorance or just a sly sense of humour which makes the word "symposium" so popular with scientists and technologists as a description of the kind of proceedings being held that week. His own knowledge of ancient Greek was strictly limited, but, on his translation, a "symposium" is nothing more or less than a Greek drinking party. It is, perhaps, not inappropriate, therefore, that at this final stage of a Symposium we should be drinking toasts. Mr. Kaberry's toast was most welcome to all members of the Society, and we greatly appreciated the terms in which it was framed.

Our membership includes scientists, technologists, practical craftsmen, and businessmen. Many of our members are all of these. The exchange of knowledge, experience, and ideas which has been taking place amongst us during the last few days has been of great value. It should have enabled the scientist to see more clearly the relation of his investigations to economic and practical considerations, and the businessman to appreciate afresh the power of scientific investigation in his affairs. Mr. Kaberry had properly enabled us to set our immediate aims and efforts against the wider perspective of national and international economic affairs.

Our concern that week had been with the problems of colouring and dyeing man-made fibres. With considerable travail man-made fibres had been successfully marketed in competition with natural fibres. During his struggle to make fibres, man had learnt respect for the silkworm and the spider. He could only hope that the ladies, having seen us grappling intently for the last two-and-a-half days with the problems of dyeing this and that, would rate their menfolk above the spider, but it was dangerous to pursue these insect analogies further. Listening to dyers talking about the difficulties of dyeing is like listening to farmers talking about the weather: there is no good weather, and almost no good fibre.

During our Symposium we have drunk more— figuratively speaking, of course— we have drunk more facts than will be fully assimilated for some weeks to come. But our discussions are not ephemeral. They will be duly recorded in print, and as such become part of the documentation and literature of our technology for future reference. The records of experience, the literature of science and technology, form one of its greatest strengths. Caliban, the monster in Shakespeare's *Tempest*, dimly recognised the source of the magic power of Prospero: the power for vengeance or creation lay in his books—

> . . . Remember
> First to possess his books; for without them
> He's but a sot, as I am, nor hath not
> One spirit to command: . . .

We have this week added some volumes to the magical literature of our technology.

When we reflect on our discussions we shall recall many pleasant memories of Buxton, and prominently among them will be remembrance of yesterday evening's charming hospitality of His Worship the Mayor of Buxton. We thank him for it most sincerely.

The current influenza problem has touched the conference. One victim is Mr. J. W. Reidy (Chairman of our Manchester Section), who was to have appeared on the toast list. In consequence of his absence, Mr. G. S. J. White finds himself at short notice with the responsibility of proposing a toast later this evening.

"OUR GUESTS"

Mr. G. S. J. WHITE (*Vice-chairman of Council*) said that everyone would be sorry that influenza had laid Mr. J. W. Reidy low, and that his witty and appropriate speech would not be available for their delectation: they would have to make do with what the Americans call a "step-in" (or perhaps it should be a *stand-in*).

Our guests that evening appeared to be of three species. Firstly were Their Worships the Mayor and the Mayoress of Buxton, closely associated with that *éminence grise* of all mayors, the Town Clerk, and his lady. It was appropriate to re-emphasise our gratitude to both gentlemen for the very personal interest that they had taken in our Symposium. Two or three years ago Buxton associated itself in an international hydropathic sisterhood with Aix-les-Bains. Greetings and visits have been exchanged and everything has been done to set in motion a sort of Schumann Plan for the advancement of water at the expense of wine and beer. How fortunate is Buxton in dealing with Aix-les-Bains to have a Mayor who once was a master plumber.

Industry in Buxton is founded solidly on (*a*) limestone and less solidly on (*b*) corsets. The latter attract me, figuratively speaking, to our next group of guests— the Ladies. Much has been said about ladies. For example, Pope wrote—

> Ladies, like variegated tulips show,
> 'Tis to their changes, half their charms we owe.

What on earth did he mean by that? One thing is certain to us dyemakers, dyers, and printers: on the ladies' blessed demand for diversity in colour, style, and fabric has been established almost our whole craft and science. We thank them and welcome them with affection to our table and the dance that follows.

Mr. Kaberry has been adequately dealt with by our President. But I must say how welcome *professional* talking has been. Mr. Kaberry must know this to be his only gathering where all colours have equal significance— blue no better than red, and neither an improvement on yellow. In dyeing it is sure that an increase from 5% to 7% strengthens the colour, but it may also darken it and make it appear much less attractive.

Lastly, we welcome most heartily our guests from overseas and particularly the lecturers, who added technological strength and variety to our Symposium— Dr. J. B. Dickey and Mr. W. H. Hindle from America, MM. J. Khachoyan and J. P. Niederhauser from France, Dr. W. Luck from Germany, and Messrs. S. Nomura and K. Tanabe from Japan. To these may be added representatives from Czechoslovakia, Holland, Russia, Sweden, and Switzerland. We thank them all for attending and so making this Symposium not only a notable scientific occasion but also such a broad and obvious display of international amity. The Society recently became a member of the International Federation of Associations of Textile Chemists and Colourists. We are therefore proud and happy to have Dr. H. Ris, Immediate Past President of the Federation, at our board tonight. He is accompanied by Mr. C. T. Speiser, representing the Schweizerischer Verein der Chemiker-Coloristen. Our Dutch sister society, the Nederlandse Vereniging voor Textielchemie, is represented by its President, Dr. F. B. Gribnau, and its Honorary Secretary, Mr. H. A. M. Boezeman. To these four we give a special welcome, and I am happy to present as leader of the international delegation my friend Dr. H. Ris. He has always worked most assiduously for international understanding, and has been a most sympathetic and valued friend of the Society.

Dr. H. RIS (*Immediate Past President of the International Federation of Associations of Textile Chemists and Colourists*), on behalf of the overseas guests, thanked the President and members of the Society for the excellent reception and the hospitality they had enjoyed. The days spent in Buxton would always be recalled as a memorable and happy time. The Symposium could be regarded as another great success, and the Society could look upon it with pleasure and pride.

The ladies should know that, when their menfolk disappeared into the Symposium lecture room, they were hearing about revolutionary progress. Chemists and colourists are in a very fortunate position, for they have devoted their lives to serving the ladies. They invent new dyes, new methods of application— naturally, all without guarantee!— new finishes, and last but not least new handles. But today we present our ladies with the latest fashion aid— man-made fibres! Can we do more for you?

I have been charged by the President of the International Federation, Dr. Luigi Sessa, with the duty of conveying to you his warmest greetings and deep gratitude for past fruitful co-operation. The importance of meetings like this is steadily increasing, because first-hand information has become a vital necessity. The Federation has therefore requested the Society to organise during 1959, in this country, the fifth International Congress. We are all sure that under your control its success is already assured, as witness the success of this gathering.

PRESENTATION OF GOLF TROPHIES

Goodall Golf Trophy miniature cups were presented to the following—

Mr. V. Davenport	Lytham Green Drive 1953
Mr. G. L. Thornton	Cavendish 1954
Mr. J. A. Hepworth	Meltham 1955
Mr. A. N. Russell	Leek 1956

WEDNESDAY AFTERNOON, 18th SEPTEMBER 1957

Chairman — Mr. Clifford Paine

The Impact of Man-made Fibres upon the Dyeing Industry*

A. H. Wilson

The largest potential field for the expansion of man-made fibres is likely to be the woollen and worsted industries, and dyeing problems will largely determine the extent to which this expansion will take place.

The paper gives a survey of the various types of problems which may arise, together with some general indication of the lines of development which are likely to be most fruitful.

During the next decade the expansion of the production of man-made fibres will exert a considerable influence on the dyeing industry, and I propose to outline what I consider will be the main forces at work without in any way attempting to go into details. Some of the problems will be essentially economic ones, where the technological problems have already been solved and where an expansion of the particular fibre concerned is taking place at the expense of other fibres. The majority of the problems will, however, be primarily technological, and a considerable start has already been made on solving many of them, as the papers to be presented at this Symposium show.

While there is likely to be a considerable expansion in the use of continuous-filament polyamide and polyester yarns, the increase in the output of staple fibres is likely to be much greater, and, for my present purpose, staple fibres can be roughly split up into the cellulosic viscose rayon staples on the one hand and the thermoplastic staple fibres on the other, including polyesters, acrylics, and cellulose triacetate. There are, of course, considerable differences in the individual behaviours of the thermoplastic fibres, but in this review they can be treated as a single group.

The problems associated with the package dyeing of continuous-filament yarns have been with us for a considerable time, and more or less satisfactory solutions have been evolved. The most recent development, which has led to a considerable expansion in end-uses, and is likely to lead to more, is the introduction of textured and crimped yarns of various types. Crimped yarns can in principle be produced from any of the thermoplastic fibres by heat-setting them in a crimped or highly twisted state. They may be dyed in the finally processed state, as packages in which the yarn has developed bulk. Since the packages are necessarily of an open nature, they are easily penetrated by dye liquors, and the dyeing process is relatively easy. It therefore seems unlikely that we shall encounter many difficult new problems which are specifically related to the continuous-filament form, and the remainder of my remarks will be devoted to staple fibres.

Until comparatively recently viscose rayon staple has been mainly used in the cotton field, but in the future the largest scope for its expansion will be in the woollen and worsted fields, while the thermoplastic staple fibres also will find most of their outlets in the same fields. Further, increasing use will be made of blends of the different fibres available. While radical improvements in the various fibres will undoubtedly be made by the fibre manufacturers from time to time, the extent to which inroads are made into the wool field by man-made fibres will depend to a large extent on the dyer, and considerable advances in technology will be required to make the foreseeable advances economically possible. Wool dyeing is in general a relatively cheap and simple process, whereas the dyeing of wool-type man-made fibres is at present costly and, owing to the swelling and the plasticity of the fibres in the dyebath, it entails very careful control. Considerable attention will therefore have to be paid to the discovery of cheaper dyes and the evolution of simpler dyeing procedures.

This latter point raises the question of the form in which the fibres should be dyed, and, since there is obviously a large freedom of choice, especially where blends are concerned, it will be convenient to consider in more detail the problems raised by carrying out the dyeing process at the various possible stages. Before doing so, I should like to make some general remarks.

It would seem that, to meet the growing complexity of textile fabrics, we cannot expect to discover a series of revolutionary dyeing methods. That is to say, the basic processes in use for natural fibres and the older man-made fibres are still with us and will remain so. There will be inventions, but for the most part we shall require a large number of refinements of dyeing processes, each of which may be small, but which in the aggregate will represent considerable advances.

The selection of dyes is necessarily becoming a much more refined business, and the grounds for choice are becoming more precise for two reasons. Firstly, the plurality of fibres in one dyebath inevitably means that the number of dyes which will either dye one component and reserve the others, or dye all to a usefully similar degree, will be fewer than the number of dyes having satisfactory properties with respect to a single fibre.

* This paper was not included in the preprints circulated before the Symposium.

Secondly, the general move towards higher fastness standards imposed by "tested-quality" and "buying-to-standard" schemes further restricts the choice of dyes.

Higher wet fastness is in general achieved by the use of bigger dye molecules, i.e. of the more slowly dyeing colouring matters. This is intensifying the overall problems of uniformity and control. Further, as compared with the dyeing of cellulosic and of protein fibres alone, the dyeing of synthetic fibres and their blends calls for more precise control of dyebath conditions. Factors such as dye concentration, temperature, pH, electrolyte concentration, rates of change of these factors, and their interplay must, especially in many cases of blend dyeing, be controlled to closer limits than hitherto. The matching of colours, when fast dyes are being applied to fibres which are difficult to dye, tends to become more hazardous. What is on cannot easily be got off, so that precision in colour matching is called for.

PARTICULAR DYEING PROCEDURES

Piece and Yarn Dyeing

The outstanding problems of piece dyeing, such as ending, listing, watering of jigger-dyed fabrics, and rope-marking and distorting of winch-dyed fabrics, have always been with us and probably always will. The prevention of these evils is achieved by the successful dyer by attention to processing details according to the precise composition, weave, and weight of his goods. The danger of processing faults of these kinds is magnified or minimised by the precise fibre composition, and discussion of methods for the successful dyeing of the newer fibres, alone and in mixture fabrics, forms a large part of the substance of the present Symposium.

Dyeing machinery is becoming more refined. The advent of synthetic fibres on the one hand and the increasing use of faster dyes on the other have led to higher dyeing temperatures and, consequently, to the use of enclosed machinery. An enclosed jigger, in which the rolls cannot be tended manually, as was normal with open machines, not only must be fitted with straighteners and crease-avoiding devices but must run absolutely true. Many dyeing machines must be made with better finishes than have been normal for wet-processing machinery. Nylon snags easily, acrylics are very weak when hot and wet; and one is not surprised to see winches in use, e.g. for nylon knitwear, made from finely buff-finished stainless steel.

Since the dyeing of fabrics or yarns is certain to meet with ever increasing difficulties as the number of blend yarns increases, there will be a considerable incentive to carrying out the dyeing process at an earlier stage, with the fibres either loose or in the form of tows, slivers, etc.

Loose or Stock Dyeing

The major difficulty in stock dyeing is to ensure adequate penetration of the fibre mass by the dye liquor while at the same time avoiding undue entanglement of the fibres, and this can be achieved only by using conditions under which the swelling of the fibres is not excessive.

At this point it is desirable to say something about spun-dyed fibres. Although the concept of mass-pigmented fibres was pioneered with viscose rayon staple, it is in principle applicable to all man-made fibres, and it has already spread in a somewhat smaller way to cellulose acetate. Melt-spinning limits the available pigments for use with polyesters and polyamides to those stable at high temperatures, but these will be extended, and spun-dyed Perlon, nylon, and Terylene have already appeared in a small range of colours.

In the apparel trades, wherever precoloration is called for as distinct from piece dyeing, spun-dyed fibres are being increasingly used. In woollens, about 80% of the production uses "loose-dyed" fibres. When a manufacturer of wool–rayon blends can get the colour required, he will use Duracols for their ease and economy of processing and their high colour fastness at low prices, rather than "dye in the wool". The Lancashire spinners are doing the same, and it is interesting to note that they are acquiring the Yorkshire dyer's art of colour-blending, and have quickly learnt to mix Duracols to produce extensive colour ranges. The Lancashire apparel trade uses mainly the fibre range 1½ denier, 1 7/16 in. to 4½ denier, 2½ in., and has greater difficulty in dyeing them as compared with coarse deniers, owing to the packing down and entanglement and the consequent spinning difficulties. Duracols have thus an added attraction for Lancashire besides their high fastness and cheapness.

As a counter to spun-dyed fibres, is it possible to develop a continuous process for stock dyeing? The advent of the rapidly dyeing Procion (ICI) dyes makes this an engineering possibility, and the Procions are of a high fastness, which makes them a suitable complement to the spun-dyed range. It should be said, however, that, where quantities of single colours are large enough to make continuous stock dyeing worth while, they become attractive to the fibre maker for spin-dyeing.

Tows, Tops, and Slivers

The direct conversion of fibre tows into tops and slivers has been known for some twenty years, but although a certain amount of Greenfield viscose rayon top is used in the worsted trade, and much development work has been carried out on other systems of tow-to-top processes, developments in this field have so far been somewhat disappointing. With the thermoplastic fibres, dyeing as a continuous tow presents many advantages, since the entanglement problems are very much less than with the dyeing of loose fibres or slubbings. There is therefore likely to be a considerable effort to overcome the present mechanical shortcomings of the various tow-to-top processes so as to ease the dyeing problems.

The dyer is also likely to meet tows rather than slubbing in the mélange trade. Two great advantages would be the greater ease of handling due to the higher linear strength and, even more valuable, the possibility of presenting the tow to

the printing roller as a flat sheet with consequent ease and uniformity of dye penetration. This should greatly improve the appearance and shorten the time required for mélanging the subsequently converted top.

The dyeing of a continuous, high-strength, uniform, and readily opened tow should lend itself to continuous methods of dye application. It should be easier to impregnate and penetrate a thin tow within a relatively small space yet with a longer dwell in the dye liquor than would be possible with a wide fabric, and dyers are no doubt prepared to experiment on these lines. There is no reason, for example, why vat dyes should not be applied to viscose rayon tow by the molten-metal principle.

CARPETS

One of the major fields for the expansion of man-made fibres is that of floor coverings of all kinds, especially tufted carpets, and here there is likely to be considerable competition between the various fibres and the various methods of coloration.

In the traditional pattern-carpet trade, the maker uses mainly dyed yarns, of which he carries large stocks in a wide range. Tufted carpets, on the other hand, call for large weights of plain colours, and at present about 60% are produced by using stock-dyed fibres, 20% are produced by using spun-dyed fibres, while about 20% are piece-dyed. Stock-dyeing of heavy deniers presents no serious difficulties either to the dyer or during subsequent spinning, but so far the progress of spun-dyed fibres in these heavy deniers (8, 12, and 15) has been limited by the unavailability of the requisite range of fibres. This state of affairs will soon be remedied, and the share of the market taken by spun-dyed fibres should increase considerably.

On the other hand, the piece-dyeing of tufted carpets is likely to remain a substantial factor in the market. The operational problems in dyeing heavy carpets are considerable, since a thick pile presents unusual problems. Simplified methods of piece-dyeing would therefore be welcomed.

CONCLUSION

In the expansion of man-made fibres into the wool field, a major obstacle to progress will be the high cost and the technical difficulty of dyeing them as compared with wool. In overcoming these handicaps, specific contributions may be expected not only from the man-made fibre industry itself but also from the dyer, the dyemaker, and the machinery maker. The progress of dye chemistry has been extensively written up during the Perkin Centenary Year, and reference to the advances made, especially in this country, could not adequately be expressed here. But mention has already been made of the Procions; these, the Cibacrons (Ciba), and other classes of chemically reactive dyes which will come along represent the beginnings of a big advance. These dyes combine a high initial diffusion rate with real chemical affinity. As distinct from diffusion–adsorption processes, their reactions with fibres take place quickly and uniformly, and are less readily reversible. We may now be looking forward to an era of quicker, and therefore cheaper, dyeing processes on the one hand, and higher dye fastness on the other. The fact that these dyeing reactions can take place at relatively low temperatures means that their application is kinder to fibres of fine denier and low wet-strength.

Other contributions have been basic dyes for acrylics and improved disperse dyes for cellulose acetate, polyamide, and polyester fibres. Enlarged ranges of really fast dyes for all these fibres are still an immediate need.

Machinery development will be largely concerned with preventing the fibres and fabrics from receiving too harsh treatment. Although the machinery makers will no doubt be undertaking a considerable amount of development work, the decision as to whether old machinery can be modified to meet new needs or whether a new process demands an improved model (or even a new mechanical approach) will inevitably rest with the dyer. The development of simple continuous processes which would minimise the entanglement problems would be a major step forward if the engineering problems could be overcome.

COURTAULDS LTD.
COVENTRY

(*MS. received 30th September 1957*)

Azo Dyes from Substituted 2-Aminothiophens

J. B. DICKEY, E. B. TOWNE, M. S. BLOOM, W. H. MOORE, B. H. SMITH JR., and D. G. HEDBERG

This paper concerns the effects of the position and the nature of substituents on the colour of azo dyes derived from 2-aminothiophens. Of primary interest is the colour shift from the red of phenylazo dyes to the greenish blue of the analogous 5-substituted 3-nitro-2-thienylazo dyes. The greenish blue of 2-amino-3-nitro-5-acyl(or aroyl)thiophen dyes is in striking contrast with the violet–red of 2-amino-5-acylthiophen dyes and the violet of dyes from 2-amino-3:5-bismethylsulphonylthiophen.

Even simple aniline coupling components afford blues to blue–greens with the 5-substituted 2-amino-3-nitrothiophens. However, progressively increased bathochromic shifts to bluish green are obtained with the following coupler types— tetrahydroquinoline, benzomorpholine, and 2-alkoxy-5-acetamidoaniline.

Dyes from 2-amino-3-nitro-5-acylthiophens, particularly, have excellent affinity for secondary cellulose acetate and give good exhaustion and level dyeing. They colour cellulose acetate deep, bright blues to greens. Dyed fabrics have superior gas-fume fastness, moderate light fastness, and good dischargeability.

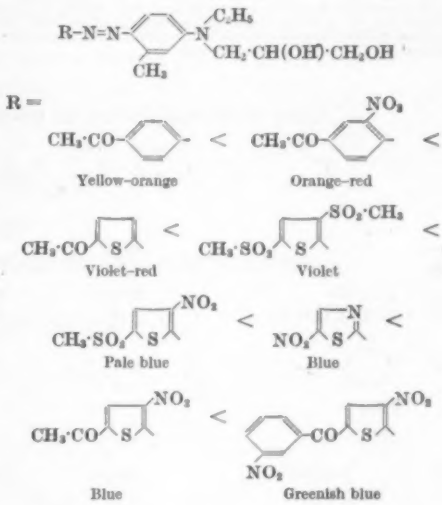
As part of a general programme to prepare blue azo dyes for cellulose acetate, a series of greenish-blue monoazo dyes was prepared by treating diazotised 5-substituted 2-amino-3-nitrothiophens with aniline coupling components, and still greener dyes were prepared with tetrahydroquinoline and benzomorpholine couplers. Bluish-green azo dyes can be obtained from certain 2-aminothiophens. These dyes are described in patents applied for from this laboratory [1].

In another recent study of azo dyes, it was found that 2-aminothiazoles containing a nitro group in the 5-position also gave blue azo dyes with simple aniline couplers [2].

It is of considerable significance, both theoretically and technically, that mononitro-substituted 2-aminothiazoles and 2-aminothiophens give blue-to-green dyes even with simple aniline couplers. The benzene analogues of these dyes are orange to red. In the phenylazo dye series a diazo component containing two nitro groups and a third negative group, such as chloro or ethylsulphamoyl, is required to give even a violet dye with the same coupler.

In the present work, the effects of different negative groups in the 3- and 5-positions of 2-aminothiophen have been studied. This paper is primarily concerned with the formation of greenish-blue dyes from 2-aminothiophens which contain a nitro group in the 3-position, and an acyl, aroyl, or methylsulphonyl group in the 5-position. The significance of this system is emphatically shown by comparison of this greenish blue with the violet of the corresponding dye from 2-amino-3:5-bismethylsulphonylthiophen, the pinkish red from ethyl 2-aminothiophen-5-carboxylate, and the violet–red from 2-amino-5-acetylthiophen.

The colour-deepening effect shown by negatively substituted 2-aminothiophen dyes is illustrated by the following series listed in the order of increasing deepening of colour—



Dyes from 2-amino-3-nitro-5-acyl(or aroyl)thiophens are blue to green on cellulose acetate and show excellent affinity even at low temperatures. These dyes have superior gas-fume fastness, wash fastness, and sublimation properties, and have moderate light fastness. The dischargeability of these dyes is also good.

A distinctive characteristic of these aminonitrothiophen dyes is that artificial light does not confer a red cast on dyed cellulose acetate: on the contrary, it produces a bathochromic shift toward green. In this respect these dyes are superior to a great many other azo dyes.

The various 2-amino-3-nitro-5-acyl(or aroyl)-thiophens were prepared by acylating 2-chlorothiophen, nitrating the resulting 2-chloro-5-acylthiophen, and then aminating the resulting 2-chloro-3-nitro-5-acylthiophen by refluxing with methanolic ammonia in the manner described by Hurd for preparing 2-amino-3-nitro-5-acetylthiophen [3, 4].

2-Amino-3-nitrothiophens substituted in the 5-position with methylsulphonyl and ethylsulphamoyl groups were prepared similarly.

The amination of 2-chlorothiophens under these conditions apparently requires the presence of a 3-nitro group*, since 2-chloro-3:5-bismethylsulphonylthiophen could not be aminated even under considerably more strenuous conditions. 2-Amino-3:5-bismethylsulphonylthiophen was therefore prepared by chlorosulphonating 2-acetamidothiophen [5] in the 3- and 5-positions, converting the chlorosulphonyl groups to methylsulphonyl groups, and hydrolysing the resulting 2-acetamido-3:5-bismethylsulphonylthiophen.

Ethyl 2-aminothiophen-5-carboxylate was prepared by reducing the corresponding nitro compound with aluminium in ether [6].

2-Amino-5-acetylthiophen was prepared by reducing 2-nitro-5-acetylthiophen with tin and hydrochloric acid.

2-Amino-3-nitro-5-acylthiophens and other substituted 2-aminothiophens were diazotised satisfactorily at 0–5°c. by addition to nitrosylsulphuric acid in either acetic acid or 50% aqueous sulphuric acid solution.

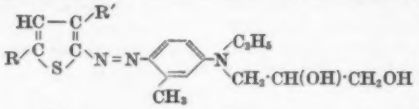
The resulting diazonium salt solutions were generally used as soon as prepared, although undue decomposition of the salt in the cold solution was not observed. Coupling was carried out at 0–5°c. by careful addition of the diazonium salt solution to a solution of the coupling component in 10% sulphuric acid or an acetic–propionic acid mixture. The dyes were obtained in yields as high as 90%. The stability of the 2-amino-3-nitro-5-acylthiophens and their diazonium salts contrasts with the relative instability of 2-aminothiophen, which does not undergo diazotisation and coupling [7].

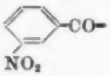
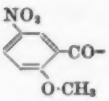
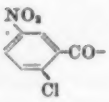
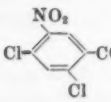
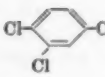
Two other negatively substituted aminothiophens, 2-aminothiophen-5-sulphonic acid [8] and ethyl 2-aminothiophen-5-carboxylate [9], have been diazotised and coupled to give red dyes with β-naphthol. The dyes of the present paper are covered by four U.S. patent applications [1].

* Hurd and Kreuz [3] have studied the behaviour towards alcoholysis and amination of various halogenated nitrothiophens and have found that, as with the benzene analogues, 2-chloro-3-nitrothiophen aminates more readily than the 5-nitro isomer.
The difficulty of aminating 2-chloro-3:5-bismethylsulphonylthiophen results not only from the lack of the specific activation conferred by an adjacent nitro group, but also from the lower activation (relative to that of the nitro group) for amination reactions conferred by the alkylsulphonyl group.

TABLE I

Effect of 3:5-Substitution on the Colour of Dyes from 2-Aminothiophens



Dye No.	R	R′	Colour on Cellulose Acetate	Dyeability*	λ_{max} (mμ.)	ϵ_{max}
1	$CH_3{\cdot}CO-$	NO_2-	Blue	Excellent	605	$3{\cdot}89 \times 10^4$
2	$(CH_3)_2CH{\cdot}CO-$	NO_2-	Blue	Excellent	604	$4{\cdot}17 \times 10^4$
3		NO_2-	Greenish blue	Good	621	$4{\cdot}00 \times 10^4$
4		NO_2-	Greenish blue	Good	623	$3{\cdot}50 \times 10^4$
5		NO_2-	Greenish blue	Good	629	$3{\cdot}16 \times 10^4$
6		NO_2-	Greenish blue	Good	631	$3{\cdot}55 \times 10^4$
7		NO_2-	Greenish blue	Good	616	$6{\cdot}84 \times 10^3$
8	$CH_3{\cdot}SO_2-$	NO_2-	Pale blue	Fair	602	$3{\cdot}90 \times 10^3$
9	$C_2H_5{\cdot}NH{\cdot}SO_2-$	NO_2-	Pale blue	Fair	578	$6{\cdot}31 \times 10^3$
10	$CH_3{\cdot}SO_2-$	$CH_3{\cdot}SO_2-$	Violet	Excellent	568	$4{\cdot}81 \times 10^4$
11	$C_2H_5O{\cdot}CO-$	H–	Pinkish red	Fair	—	—
12	$CH_3{\cdot}CO-$	H–	Violet–red	Good	525	$3{\cdot}25 \times 10^4$

* In this paper, *dyeability* means depth or extent of dyeing under the conditions described in the section on *Dyeing and Testing*.

Discussion

DYES FROM 3:5-DISUBSTITUTED 2-AMINOTHIOPHENS

A series of 3:5-disubstituted 2-aminothiophen dyes incorporating a typical aniline coupler are listed in Table I. The colour on cellulose acetate, dyeability, and spectral data are included. In general, these dyes give bright colours on cellulose acetate. The 3-nitro-5-acyl(or aroyl)-2-thienylazo dyes give especially deep colours as well. From a consideration of Table I it can be concluded that with an aniline coupler—

(1) The 3-nitro-5-acyl-2-thienylazo dyes are blue and have excellent dyeability (dyes 1 and 2— λ_{max} 605, 604 mμ.).

(2) The 3-nitro-5-nitroaroyl-2-thienylazo dyes are greenish blue (dyes 3–6— λ_{max} 621, 623, 629, 631 mμ.). Dye 7, which does not contain a nitro group in the benzoyl substituent, is also greenish blue. It dyes less deeply, however. This property may be related to its low ε_{max} value.

(3) The 3-nitro-5-nitroaroyl-2-thienylazo dyes are noticeably affected by chloro substituents in the nitrobenzoyl group. Relative to dye 3, they exhibit a bathochromic shift of about 10 mμ., giving still greener colours (dyes 5 and 6), whereas a methoxyl group has only a slight effect (dye 4).

(4) The 5-substituted 3-nitro-2-thienylazo dyes containing a 5-methylsulphonyl or 5-ethylsulphamoyl group (dyes 8 and 9) are pale blue. Compared with dye 1, for example, they have poor dyeability and show a hypsochromic effect due to the replacement of the acetyl by a sulphonyl or sulphamoyl group.

(5) The 3:5-bismethylsulphonyl-2-thienylazo dye (No. 10) is violet and has excellent dyeability. Thus, although the methylsulphonyl group confers only slight hypsochromism relative to the acetyl group (cf. λ_{max} of dyes 1 and 8), it confers considerable hypsochromism relative to the nitro group, the λ_{max} being shifted more than 30 mμ. (dyes 8 and 10)*.

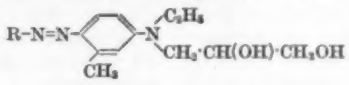
From the above considerations it follows that the most pronounced bathochromic effect shown in dyes from the 2-aminothiophens is conferred by the 3-nitro-2-thienyl group. Although in this series only 3-nitro-2-thienylazo dyes are blue to greenish blue, relative to their phenylazo analogues all negatively substituted 2-thienylazo dyes display a bathochromic effect. This bathochromism is illustrated in Table II.

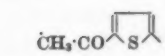
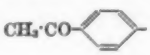
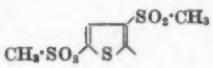
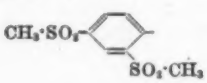
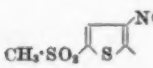
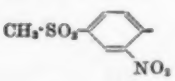
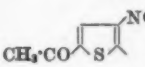
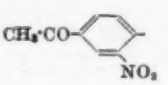
A comparison of the pairs of thiophen and benzene dye analogues in Table II reveals this bathochromism. Dyes having moderately polar substituents in the thiophen ring show a bathochromic shift of 60–70 mμ. in λ_{max} relative to their benzene analogues (dyes 3 and 4, 1 and 2). Dyes

* A somewhat similar effect of the alkylsulphonyl group compared with the nitro group is observed in the analogous azo dyes from 2-amino-5-butylsulphonylthiazole and 2-amino-5-nitrothiazole. There is a hypsochromism of more than 40 mμ. The slight hypsochromism of the sulphonyl group relative to the acetyl group is also exhibited in the benzene series by the analogous dyes from *p*-methylsulphonylaniline and *p*-aminoacetophenone (λ_{max} 450 and 457 mμ. respectively).

TABLE II

Comparison of Dyes from 2-Aminothiophens and their Benzene Analogues



Dye No.	R	Colour on Cellulose Acetate	Dyeability	λ_{max} (mμ.)	ε_{max}
1		Violet–red	Good	525	$3{\cdot}25 \times 10^4$
2		Yellow–orange	Good	457	$3{\cdot}35 \times 10^4$
3		Violet	Excellent	568	$4{\cdot}81 \times 10^4$
4		Red	Good	510	$3{\cdot}66 \times 10^4$
5		Pale blue	Fair	602	$3{\cdot}90 \times 10^3$
6		Red	Good	496	$3{\cdot}26 \times 10^4$
7		Blue	Excellent	605	$3{\cdot}89 \times 10^4$
8		Red	Good	503	$3{\cdot}18 \times 10^4$

having a highly polar substituent, such as the nitro group, in the thiophen ring show a much greater bathochromic effect, the λ_{max} being shifted more than 100 mμ. (dyes 5 and 6, 7 and 8).

The λ_{max} shift exhibited in these 2-thienylazo dyes would suggest that the thiophen ring is more polarisable than the benzene ring. The enhanced λ_{max} shift caused by the nitro group (which is highly electron-attracting) would seem to confirm this inference. This polarisability of the thiophen ring is undoubtedly fundamental to the mechanism whereby blue and green colours ensue from such relatively simple azo dyes.

The bathochromic effect exhibited by the 2-thienylazo dyes relative to their benzene analogues can perhaps be best envisaged by comparison of their colours on secondary cellulose acetate. For example, the azo dye from 2-amino-3-nitro-5-acetylthiophen is blue, whereas the corresponding azo dye from its benzene analogue, 4-amino-3-nitroacetophenone, is red (dyes 7 and 8).

Since in these analogues the substituents and their positions are alike, this colour shift must be attributed in part to the relatively greater interaction of these groups with the thiophen ring than with the benzene ring. This greater interaction results from the inherent properties of the thiophen ring itself rather than from those of the substituents.

EFFECT OF COUPLING COMPONENTS ON COLOUR

Generally, the colour of azo dyes depends on the nature of both the diazo and the coupling components. As was shown in Table I, the nature of the substituents in the 2-aminothiophens has a profound effect on the colour of the resulting azo dyes. Also, the nature of the substituents in the series of coupling components used has a decided effect on the colour of these dyes. Thus, as in other azo dye series, the following coupler types afforded with the 2-aminothiophens a bathochromic shift in the following order: aniline < tetrahydroquinoline < benzomorpholine < 2-alkoxy-5-acetamidoaniline.

This resulting colour shift (about 45 mμ.) of 3-nitro-5-acetyl-2-thienylazo dyes from blue toward green is shown in Table III and discussed later. The progressively deepening colour of this series of dyes as measured spectrophotometrically in methanol solution was also shown on cellulose acetate.

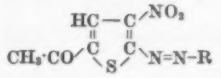
The progressively colour-deepening effect of this series of coupling components is demonstrated by other azo dyes as well. A comparison of λ_{max} shifts for several diazo components is illustrative. As shown in Table III, 3-nitro-5-acetyl-2-thienylazo dyes are shifted about 45 mμ. in λ_{max} values going from the aniline coupler to the 2-alkoxy-5-acetamidoaniline (dyes 1 and 4). The colours on cellulose acetate are, as a result, shifted from blue to blue–green.

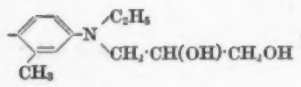
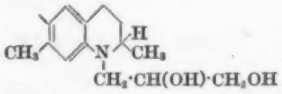
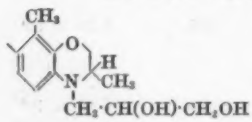
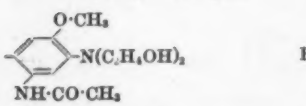
The corresponding 3-nitro-5-*m*-nitrobenzoyl-2-thienylazo dyes are somewhat greener, but the λ_{max} shift is again about 45 mμ. In comparison, 5-nitro-2-thiazolylazo dyes show a λ_{max} shift of 33 mμ., the colours of the corresponding dyes on cellulose acetate being blue and greenish blue. The corresponding λ_{max} shift for 2:4-dinitro-6-ethylsulphamoylphenylazo dyes is still less, being 31 mμ. The colours on cellulose acetate are blue–violet and blue respectively.

In the dyes from these various diazo components the λ_{max} shift effected presumably results from increasing electron release, or polarisability, of the couplers. The extent of the shift probably cannot be accounted for simply by the increased mass of the molecule, nor by steric effects of the coupler substituents.

TABLE III

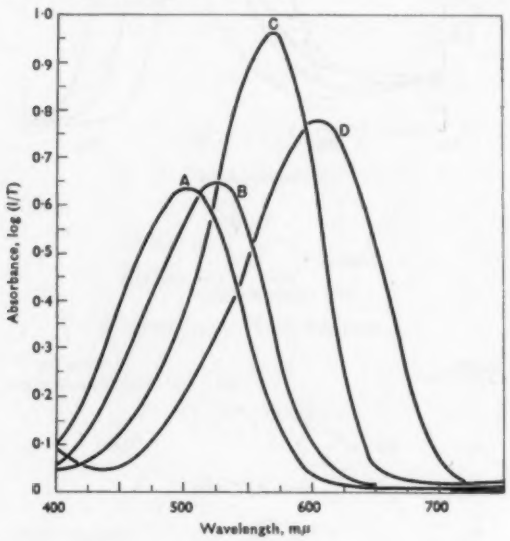
Effect of Coupling Component on Colour

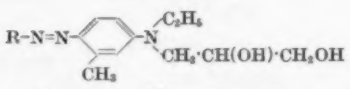


Dye No.	R	Colour on Cellulose Acetate	Dyeability	λ_{max} (mμ.)	ε_{max}
1		Blue	Excellent	605	$3{\cdot}89 \times 10^4$
2		Greenish blue	Excellent	629	$4{\cdot}59 \times 10^4$
3		Greenish blue	Good	630	$2{\cdot}09 \times 10^4$
4		Blue–green	Good	652	$3{\cdot}79 \times 10^4$

That the relative electron-release properties of the coupler must be important to the colour of azo dyes is demonstrated by the hypsochromic shifts produced with aniline couplers having electronegative groups substituted either in the phenyl ring or in the *N*-alkyl group*. For example, couplers derived from *N*-fluoroalkylanilines[1,9] produce violet instead of blue 2-thienylazo dyes.

Similarly, the electron-attracting properties of the diazo component are of importance in the relative λ_{max} shift encountered in the dyes discussed above. Apparently the 3-nitro-2-thienyl system, containing e.g. a 5-acetyl or a 5-*m*-nitrobenzoyl group, has sufficient polarisability, or electron attraction, for the λ_{max} shift for the coupler series to be about 45 mμ. The 5-nitro-2-thiazolyl system is somewhat less polarisable, showing a λ_{max} shift of 33 mμ.





(Concn. 2·0 × 10^{-5} M. in methanol)

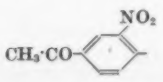
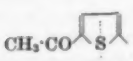
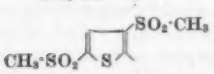
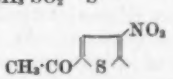
Curve	R	Colour on Cellulose Acetate
A		Red
B		Violet–red
C		Violet
D		Blue

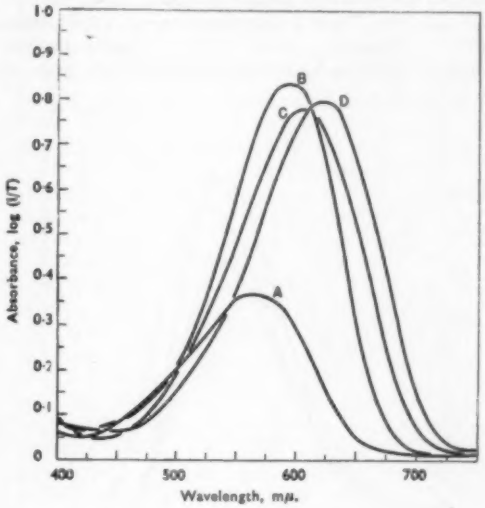
FIG. 1— Relative Colour-deepening Effect of Negative Groups in 2-Thienylazo Dyes

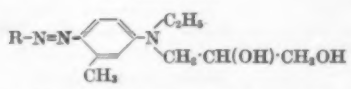
* *N*-(2:2:2-Trifluoroethyl)aniline, for example, is so weakly basic that it is insoluble in 5% hydrochloric acid solution. *N*-Fluoroalkylanilines in which the fluorine atoms are farther removed from the nitrogen atom more closely resemble their unfluorinated analogues in basicity and effect smaller hypsochromic shifts than *N*-(2:2:2-trifluoroethyl)aniline.

Surprisingly, the highly negatively substituted system, 2:4-dinitro-6-ethylsulphamoylphenylazo, has the least response to increased electron release by the coupler. The λ_{max} shift from the aniline coupler to the 2-alkoxy-5-acetamidoaniline coupler is not only the least (31 mμ.) of those considered here; but, further, the 2-alkoxy-5-acetamidoaniline causes no λ_{max} shift relative to the tetrahydroquinoline coupler.

ABSORPTION SPECTRA

Fig. 1 shows the absorption spectra of a series of dyes derived from a simple aniline coupler and 4-amino-3-nitroacetophenone, 2-amino-5-acetylthiophen, 2-amino-3:5-bismethylsulphonylthiophen, and 2-amino-3-nitro-5-acetylthiophen. In accordance with the shift toward longer wavelengths, the dyes are red, violet–red, violet, and blue respectively. The relative colour-deepening effect produced by increasingly negative groups in





(Concn. 2·0 × 10^{-5} M. in methanol)

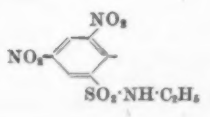
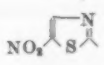
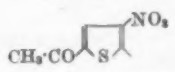
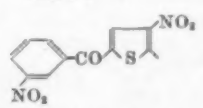
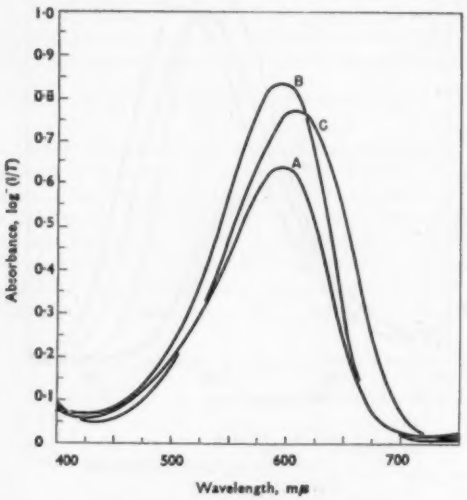
Curve	R	Colour on Cellulose Acetate
A		Blue–violet
B		Blue
C		Blue
D		Greenish blue

FIG. 2— Comparison of Colours of Phenylazo, 2-Thiazolylazo, and 2-Thienylazo Dyes incorporating an Aniline Coupling Component

the 2-aminothiophens is thus demonstrated. Further, since the same negative groups are present, comparison of the benzene analogue of 2-amino-3-nitro-5-acetylthiophen indicates the intrinsic bathochromism exhibited by the thiophen nucleus.

Fig. 2 shows the absorption spectra of a series of dyes made from the same aniline coupler and 2-ethylsulphamoyl-4:6-dinitroaniline, 2-amino-5-nitrothiazole, 2-amino-3-nitro-5-acetylthiophen, and 2-amino-3-nitro-5-*m*-nitrobenzoylthiophen. Correspondingly, the dyes are blue–violet, blue, blue (slightly greener), and greenish blue on cellulose acetate and in methanol solution. This series shows that the above 2-aminothiophens afford significantly greener dyes than 2-amino-5-nitrothiazole or an aniline substituted with three highly negative groups.

The absorption spectra of another series of dyes are shown in Fig. 3. By using a tetrahydroquinoline coupler to produce bathochromism, a blue dye was obtained from 2-ethylsulphamoyl-4:6-dinitroaniline. However, even with a simple aniline coupler, 2-amino-3-nitro-5-acetylthiophen gave a deeper and somewhat greener blue dye. With the same aniline coupler, 2-amino-5-nitrothiazole also gave a deeper blue dye.



(Concn. 2·0 × 10^{-5} M. in methanol)

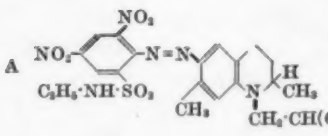
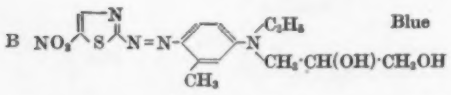
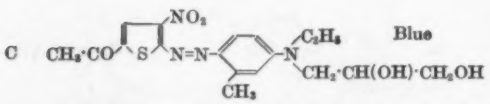
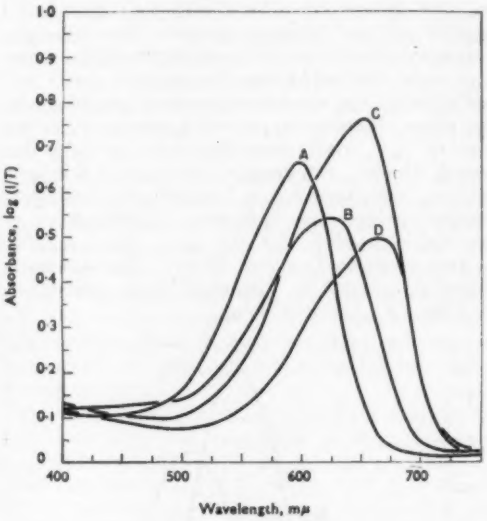
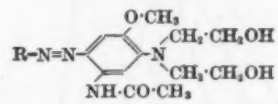
Curve	Dye	Colour on Cellulose Acetate
A		Blue
B		Blue
C		Blue

FIG. 3— Colour-deepening of 2-Thiazolylazo and 2-Thienylazo Dyes relative to Phenylazo Dyes





(Concn. 2·0 × 10^{-5} M. in methanol)

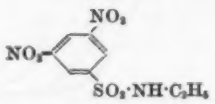
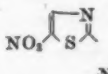
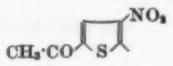
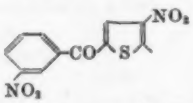
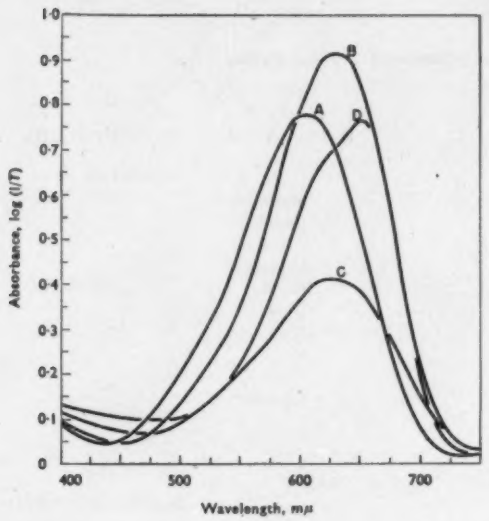
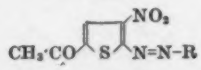
Curve	R	Colour on Cellulose Acetate
A		Blue
B		Greenish blue
C		Blue–green
D		Bluish green

FIG. 4— Comparison of Colours of Phenylazo, 2-Thiazolylazo, and 2-Thienylazo Dyes incorporating a Bathochromic-conferring Coupler

NN - Bis - 2′ - hydroxyethyl - 2 - methoxy - 5 - acetamidoaniline, a coupler generally conferring an even greater bathochromic effect than the tetrahydroquinoline coupler, nevertheless gave a dye of about the same colour (Fig. 4) with the negatively substituted diazo component. As before, however, the deepening of colour was pronounced in the case of the corresponding dyes from 2-amino-3-nitro-5-acetylthiophen and 2-amino-3-nitro-5-*m*-nitrobenzoylthiophen: these dyes are decidedly greener. The dye from 2-amino-5-nitrothiazole is intermediate between the two types, being greenish blue.





(Concn. 2·0 × 10^{-5} M. in methanol)

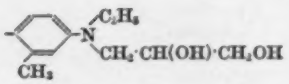
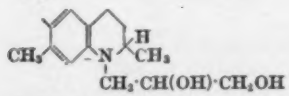
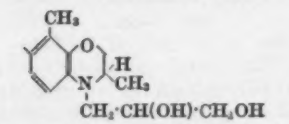
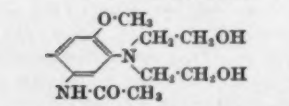
Curve	R	Colour on Cellulose Acetate
A		Blue
B		Greenish blue
C		Greenish blue
D		Blue–green

FIG. 5— Effect of Coupling Component on the Colour of Dyes from 2-Amino-3-nitro-5-acetylthiophen

Fig. 5 shows the absorption in order of increasing wavelength of the dyes from a series of couplers with 2-amino-3-nitro-5-acetylthiophen. The increasing bathochromic effect of these couplers is in the following order: aniline < tetrahydroquinoline < benzomorpholine < 2-alkoxy-5-acetamidoaniline.

The work described in this paper demonstrates the remarkable bathochromic effect observed in dyes from 2-amino-3-nitro-5-acyl(or aroyl)thiophens relative to their benzene analogues. This effect is even more pronounced than in dyes from 2-amino-5-nitrothiazoles. A blue phenylazo dye is obtained only when the diazo component contains such substituents as three highly negative groups, including two nitro, and the coupler is one conferring a pronounced bathochromic effect. Hence, the bathochromism of the 3-nitro-5-acyl(or aroyl)-2-thienyl group may require a special mechanism involving the thiophen ring for its explanation.

DYEING AND FASTNESS PROPERTIES [11]

The dyeing properties of dyes from 2-amino-3-nitro-5-acyl(or aroyl)thiophens are generally good. These dyes have good affinity for cellulose acetate, giving deep, level colorations with good exhaustion of the dyebath in most cases. An outstanding characteristic of these dyes is that they give level dyeings at low temperatures (70–80°C.), making them adaptable to jig dyeing.

These dyes have good fastness to washing and sublimation, excellent fastness to dry cleaning, and fair fastness to perspiration and wet-pressing. They show outstanding resistance to atmospheric or gas-fume fading, but have only moderate light fastness. In addition, they have good discharge properties.

Dyeing and fastness properties of the 3-nitro-5-acyl-2-thienylazo dyes are in general somewhat better than those of the corresponding 3-nitro-5-aroyl-2-thienylazo dyes. The dyes in which the 5-aroyl group has a nitro substituent or chloro and nitro substituents are considerably more satisfactory than the unsubstituted 5-aroyl dyes.

Dyes from 2-amino-3:5-bismethylsulphonylthiophen do not exhibit a bathochromic shift (relative to the benzene analogue) as pronounced as that exhibited by dyes from 2-amino-3-nitro-5-acyl(or aroyl)thiophens. Moreover, the dye from 2-amino-3:5-bismethylsulphonylthiophen and *N*-ethyl-*N*-(2:3-dihydroxypropyl)-*m*-toluidine is violet, not blue. This dye, however, is noteworthy in its excellent affinity and intensity of colour.

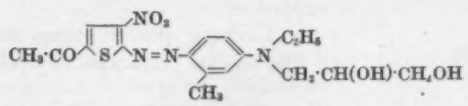
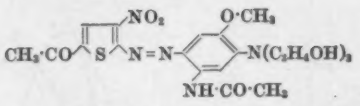
The colour shift produced by the various couplers used is much more pronounced than variations produced in dyeing and fastness properties. Thus, the good dyeing and fastness properties exhibited by azo dyes from 2-amino-3-nitro-5-acetylthiophen and *N*-ethyl-*N*-(2:3-dihydroxypropyl)-*m*-toluidine, a simple aniline coupler, are also shown by the corresponding dyes incorporating other couplers. This fact is illustrated in Table IV by the first two dyes. Although the 2-methoxy-5-acetamidoaniline coupler confers a much greener colour on the 3-nitro-5-acetyl-2-thienylazo dyes than the simple aniline coupler does, the properties are essentially the same. The corresponding dye (No. 2, Table III) from the tetrahydroquinoline coupler is intermediate in colour, giving a greenish blue on cellulose acetate. This dye also has excellent affinity and gives deep, bright dyeings, but it shows poorer exhaustion.

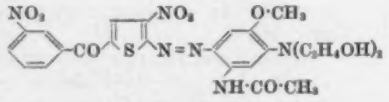
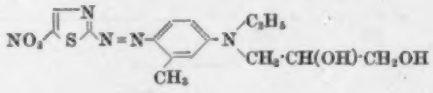
The dyeing and fastness properties of three of these thiophen dyes may be compared with those of the corresponding 2-amino-5-nitrothiazole dye by reference to Table IV. This thiazole dye shows the same light and gas-fume fastness as, but generally better dyeing properties than, the thiophen dyes described in this paper.

A notable characteristic of the blue–green aminonitrothiophen dyes is that they are not reddened by artificial light; in this respect they are superior to the thiazole dyes.

TABLE IV

Dyeing and Fastness Properties of 2-Thienylazo and 2-Thiazolylazo Dyes

Test		
Light fastness ...	Moderate	Moderate
Gas-fume fastness ...	Excellent	Good
Rate of dyeing (70°C.)	Good	Good
Dischargeability ...	Moderate	Moderate
Sublimation	Good	Good
Rubbing	Good	Good
Dry cleaning	Excellent	Excellent
Wet pressing	Fair	Poor
Perspiration	Poor	Fair
No. 2 wash test (120°C.) [11]	Satisfactory	Satisfactory

Test		
Light fastness ...	Moderate	Moderate
Gas-fume fastness ...	Good	Excellent
Rate of dyeing (70°C.)	Fair	Excellent
Dischargeability ...	Moderate	Excellent
Sublimation	Good	Excellent
Rubbing	Good	Excellent
Dry cleaning	Excellent	Excellent
Wet pressing	Fair	Excellent
Perspiration	Fair–good	Excellent
No. 2 wash test (120°C.) [11]	Satisfactory	Satisfactory

Experimental

PREPARATION OF INTERMEDIATES

The preparation of the 2-amino-3-nitro-5-acyl(or aroyl)thiophens and other 3:5-disubstituted 2-aminothiophens is to be the subject of another paper. The following syntheses, adapted from Hurd and Kreuz [3], are typical—

2-AMINO-3-NITRO-5-ACETYLTHIOPHEN— A solution of 50 g. (0·42 mole) of 2-chlorothiophen and 33 g. (0·42 mole) of acetyl chloride in 300 ml. of hexane was treated portionwise with 56 g. (0·42 mole) of aluminium chloride at 40°C. over a period of 40 min. The reaction was mild, and a purple complex separated. After the mixture had been stirred for 1 hr., the hexane was decanted off, and the dark residue was decomposed by adding ice. Steam distillation yielded 48 g. of a white, low-melting solid, which was washed twice with cold pentane to give 36 g. (56%) of 2-chloro-5-acetylthiophen, m.p. 44–46°C.

A mixture of 52 g. (0·74 mole) of fuming nitric acid and 150 ml. of concentrated sulphuric acid cooled to 0°C. was treated portionwise during 1 hr. with 100 g. (0·63 mole) of 2-chloro-5-acetylthiophen. After stirring for 1 hr. more at 10–20°C., the reaction mixture was poured on to ice. The yellow–buff precipitate was collected on a filter, washed until neutral, and dried. The yield of crude product was 124 g. (97%), m.p. 67–75°C. Two crystallisations from *cyclo*hexane gave 80·5 g. (63%) of 2-chloro-3-nitro-5-acetylthiophen as yellow needles, m.p. 68–81°C. Recrystallisation from ethyl alcohol raised the melting point to 75–84°C.

A solution of 14·5 g. (0·07 mole) of 2-chloro-3-nitro-5-acetylthiophen and 55 ml. of 28% ammonium hydroxide in 300 ml. of methanol was refluxed for 1 hr. The reaction mixture was cooled and filtered. The purplish precipitate was washed and dried to yield 6·5 g. of product. An additional 1·3 g. was obtained by concentration of the mother liquors. The combined products, 7·8 g. (60·8%), melted at 224–227°C. Two crystallisations from acetic acid gave 2-amino-3-nitro-5-acetylthiophen as a brown–yellow solid, m.p. 227–228°C.

COUPLERS— The various couplers used in preparing these azo dyes have been previously described: *N*-ethyl-*N*-(2:3-dihydroxypropyl)-*m*-toluidine [2], *N*-(2:3-dihydroxypropyl)-2:7-dimethyl-1:2:3:4-tetrahydroquinoline [12], *N*-(2:3-dihydroxypropyl)-2:5-dimethylbenzomorpholine [12]. *NN*-Bis-2[1]-hydroxyethyl-2-methoxy-5-acetamidoaniline, a well known commercial intermediate, was also used.

PREPARATION OF DYES

DIAZOTISATION— The various substituted 2-aminothiophens were all diazotised in nitrosylsulphuric acid. The diazotisation of 2-amino-3-nitro-5-acetylthiophen is typical.

Nitrosylsulphuric acid was prepared by adding 1·52 g. (0·022 mole) of sodium nitrite portionwise to 10 ml. of concentrated sulphuric acid with stirring while allowing the temperature to rise to

65°C. but no higher. The solution was then cooled to 5°C., and 20 ml. of a mixture of 6 ml. of propionic acid and 34 ml. of acetic acid was added dropwise with stirring, allowing the temperature to rise to 15°C. but no higher. The reaction mixture was then cooled to 0–5°C., and 3·72 g. (0·02 mole) of 2-amino-3-nitro-5-acetylthiophen was added portionwise while stirring, after which the remaining 20 ml. of the propionic–acetic acid mixture was added at 0–5°C. Stirring was continued at this temperature for 2 hr., and then 0·2 g. of urea was added to destroy excess of sodium nitrite. The clear diazonium solution was then used.

COUPLING—To a stirred solution of 0·84 g. (0·004 mole) of *N*-ethyl-*N*-(2:3-dihydroxypropyl)-*m*-toluidine in 7 ml. of 10% sulphuric acid, at 0–5°C., was added 10 ml. (0·004 mole) of the diazonium solution. Coupling was allowed to proceed for 15 min., and then the reaction mixture was poured into 200 ml. of cold water with stirring. The precipitated dye was allowed to stand for 1 hr., and then was filtered, washed neutral, and dried.

The dye weighed 1·14 g. (70%) and was a dark powder. It dyed cellulose acetate deep blue. It had good light fastness and excellent gas-fume fastness on cellulose acetate fabric, and under artificial light there was no change in colour toward red. On cellulose acetate it gave fairly good discharge prints.

DYEING AND TESTING

Dyeings in this work were made on 10-g. samples of a jersey fabric knitted from dull secondary cellulose acetate filament yarn.

Dispersions of the dyes were prepared by grinding 33·3 mg. of dye on a metal plate with 5 ml. of 5% aqueous sodium ligninsulphonate solution and 15 ml. of 0·2% aqueous Igepon T (G) solution. Dyeings were carried out by washing the dispersion into the dye pot and making up the dyebath to 300 ml. with demineralised water. The previously wetted-out fabric was placed in the cold dyebath, and the temperature raised to 80°C. in 20 min. Dyeing was continued for 1 hr. with the necessary agitation, and the fabric was then rinsed and air-dried. No finish was used.

All fastness tests were carried out in accordance with the procedures of the American Association of Textile Chemists and Colorists[11].

DETERMINATION OF ABSORPTION SPECTRA

The absorption spectra were obtained with a Cary recording spectrophotometer (Model 14) using a 1-cm. cell. The dyes were dissolved in anhydrous methanol, and the concentration used was $2{\cdot}0 \times 10^{-5}$ mole per litre. The dyes used in the spectroscopic study were not given rigorous purification. However, careful purification by chromatography did not affect λ_{max} values. The absorbance, and hence ε_{max} values, of the dyes were increased on purification; therefore, use of the reported ε_{max} values may not be of great significance in evaluating these dyes.

* * *

The authors wish to thank Mr. Marshall Otis, of the Research Laboratories, for the spectrophotometric determinations and for helpful suggestions.

RESEARCH LABORATORIES
TENNESSEE EASTMAN CO.
DIVISION OF EASTMAN KODAK CO.
KINGSPORT
TENNESSEE
U.S.A.

(*MS. received 28th March 1957*)

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[1] U.S. Patents applied for by the Eastman Kodak Co. (claims accepted).
[2] Paper presented at the 131st Meeting of the American Chemical Society (April 1957).
[3] Hurd and Kreuz, *J. Amer. Chem. Soc.*, **74**, 2965 (1952).
[4] Kreuz and Hurd (to Texas Co.), *USP* 2,642,440 (1953).
[5] Hurd and Moffat, *J. Amer. Chem. Soc.*, **73**, 1613 (1951).
[6] Dann, *Ber. deutsch. chem. Ges.*, **76**, 419 (1943).
[7] Stadler, *ibid.*, **18**, 2316 (1885).
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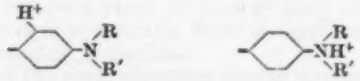
[9] Dann, *Chem. Ber.*, **82**, 72 (1949).
[10] Dickey *et al.*, *Ind. Eng. Chem.*, **45**, 1730 (1953).
[11] AATCC, *Technical Manual and Yearbook*, **32**, 72–97 (1956).
[12] McNally and Dickey (to Eastman Kodak Co.), *USP* 2,342,678 (1944); Dickey and McNally (to Eastman Kodak Co.), *USP* 2,391,886 (1946).

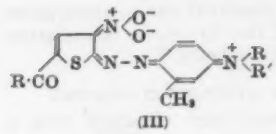
Discussion

Dr. L. PETERS: Why put the charged hydrogen H^+ in the *meta* position of a benzene ring, instead of on the nitrogen atom, e.g. I instead of II?

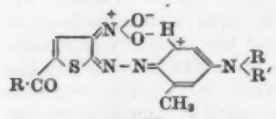


(I) (II)

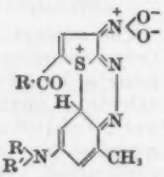
Dr. DICKEY: This question refers to the possible resonance structures postulated for the 3-nitro-2-thienylazo dyes. Although this subject was not discussed in the paper itself, slides presenting these structures were included to explain the unusual colour of the dyes. These resonance structures do not, of course, involve the addition of a proton to the ground-state structure as implied in the question. Actually, the charges shown on the resonance structures represent charge separation due to the electronic displacement in the molecule when activated by the absorption of light. Such resonance structures are commonly used to represent the resulting excited-state structures. The resonance structure III, shown with the positive charge on the dialkylamino group, resembles the more conventional excited-state structure, whereas the structure IV, with the positive charge on the *meta* position of the benzene ring, is not only a variant of the above resonance structure but also a precursor to the postulated cyclic excited-state structure V.



(III)

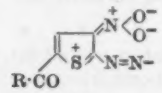


(IV)



(V)

Prof. W. BRADLEY: Is resonance structure VI likely to explain the blue colour of some of the dyes (cf. Methylene Blue, VII)?



(VI)

(VII)

Dr. DICKEY: The resonance structure VI and the structure extending the electron displacement to the 5-position are perhaps the most important polarised structures causing the aromaticity of the thiophen ring. However, we do not think that such forms contribute significantly to the absorption by these azo dyes of energy in the visible region. Bradley's structure (VI) would suggest that any substituent in the 2-position of 3-nitro-5-acetylthiophen would cause high coloration. Further, this structure does not allow extension through the azo group of electron displacements originating in the coupler constituent. Nor could the hypsochromic and bathochromic shifts effected by use of various couplers in dyes from 2-amino-3-nitro-5-acetylthiophen be explained. Structure III is an example showing participation by the 2-phenylazo group.

Mr. R. K. FOURNESS: What is the effect on properties other than colour, e.g. fastness to light and washing, of replacing a benzene nucleus by a thiophen ring?

Dr. DICKEY: The thiophen dyes described in this paper show no general trend of superior or inferior properties compared with their benzene analogues. Although the wash fastness is the same in the comparisons we have made, the light fastness is variable. Thus, the 3-nitro-5-acetylthienylazo and the 3-nitro-5-methylsulphonylthienylazo dyes, for example, are faster to light than their phenylazo analogues, whereas the 3:5-bismethylsulphonylthienylazo dye has a lower light fastness. Dyeability also is variable, as is shown in Table II.

Mr. A. MURRAY: In the paper prominence is given to blue dyes derived from 2-aminothiophens. Are the red dyes from 2-aminothiophens of any commercial interest, or do they offer no advantage over well known red disperse dyes of the substituted aminoazobenzene type?

Dr. DICKEY: The few red to violet dyes from 2-aminothiophens that have been made generally do not have improved properties over the red phenylazobenzene dyes. In view of their higher cost they therefore offer no advantage.

Mr. E. STEAD: It would be interesting to know the effect of a nitro group in the 5-position of the thiophen ring.

Dr. DICKEY: Dyes from 2-amino-3:5-dinitrothiophen are greener than the corresponding dyes from 2-amino-3-nitro-5-acetylthiophen. Thus, the replacement of the acetyl group by a nitro group does result in the expected bathochromic effect. The dyes from both 2-amino-3-nitrothiophen and 2-amino-5-nitrothiophen are also being studied. It would not be unexpected that they would resemble in colour the blue 2-amino-5-nitrothiazole dyes.

THURSDAY MORNING, 19th SEPTEMBER 1957

Chairman — Mr. H. CUNLIFFE

New Method for the High-temperature Dyeing of Acrylic Fibres

J. KHACHOYAN and J. P. NIEDERHAUSER

A new method of dyeing polyacrylonitrile fibres at high temperatures, in the presence of hydroxylamine sulphate, is described in detail. The hydroxylamine salt seems to modify the nitrile groups into new functions containing amino groups, which confer on the fibre affinity for soluble and insoluble dyes of different classes— acid, direct, metal-complex, phthalocyanine, etc.

I— Introduction

The coloration of the acrylic fibres has been one of the most intensively studied of dyeing problems during the past decade. Indeed, the great majority of dyes applied by the usual dyeing methods have little or no affinity for them. But as these fibres possess very attractive and interesting properties, it was necessary to look for new methods and techniques of dyeing, in order to ensure their future development.

Four lines of attack could be followed—

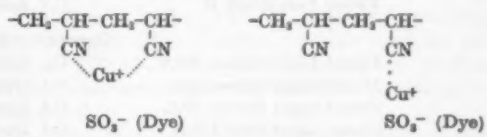
(1) Addition of pigments to the polymer before spinning: this method has great known disadvantages and has not been developed industrially so far.

(2) Partial modification of the polymer or addition of certain derivatives, i.e. copolymers, to increase either the accessibility of the fibre to the dye molecule, or its affinity for the dyes by introducing new chemical functions. Numerous patents have described the preparation of such modified acrylic polymers, and the most important example is the Acrilan fibre of the Chemstrand Corpn. (U.S.A.), which is nowadays produced industrially.

(3) Development and improvement of existing ranges of dyes: the most typical example is the range of basic dyes, in which certain old brands have shown good affinity and fastness on acrylic fibres, and which has been completed by new products, notably in the Sevron (DuP) and Deorlene (Ciba) ranges.

(4) Development of new dyeing methods allowing existing dyes to be applied to acrylic fibres. Thus the recent high-temperature technique (above 100°C.) has given better results and heavier dyeings with selected disperse dyes, by increasing their corresponding uptake by the acrylic fibre. A more or less complete range of hues of good all-round fastness is now available from the different dye-manufacturing companies.

One of the most surprising dyeing developments in recent years was the cuprous-ion method[1], discovered in 1951 in the U.S.A. and applied initially to dynel, which permits acid dyes to be applied to acrylic fibres. Among the many reducing agents which have been proposed, hydroxylamine sulphate has been regarded as one of the most interesting, and its use was patented[2] in 1951. The exact nature of the link between the cuprous ions and the fibre is not yet well established, and for simplicity the mechanism can be represented by the following possible schemes—



It is clear that the basis of this mechanism is the introduction of positive charges into the fibre, which permit the subsequent attachment of dye anions.

Instead of producing cuprous ions in the dyebath by reduction of cupric ions, we thought of using copper-complex dyes, which in the presence of a suitable reducing agent might be modified in such a way that the dyeing of the acrylic fibre would become possible. We obtained positive results with such copper-complex dyes in the absence of cupric ions, but only in the presence of hydroxylamine or one of its salts as reducing agent, and only by dyeing at high temperatures.

This new method of dyeing acrylic fibres at high temperatures has already been briefly described[3] for the copper complexes of monosulphonated *oo'*-dihydroxymonoazo dyes. We have found, however, that this method can be applied also to copper-complex polysulphonated polyazo dyes such as—

Diazol Light Blue 3JLN (C.I. Direct Blue 98)
Diazol Light Brown BRN (C.I. Direct Brown 95)
Diazol Light Brown 8RL (C.I. Direct Brown 112)

and to both soluble and insoluble derivatives of copper phthalocyanine.

By analogy, we applied the method to chromium- and cobalt-complex dyes, both the 1:1 complexes (Inochromes) and the corresponding 2:1 complexes (Neutrichromes). Surprisingly, we obtained positive results, and found that the 2:1 complex dyes possess very high affinities for acrylic fibres. This is contrary to what has been mentioned in the patent[3], according to which no dyeing occurs with chromium-complex dyes.

Further experiments showed that even dyes containing no metal atom possess a much higher affinity for acrylic fibres when applied under the above conditions.

TABLE I

Tinctorial Value and Light Fastness of 2% Dyeings on Orlon 42

Dye	*Colour Index* No.	Tinctorial Value	Light Fastness
	1:1 METAL-COMPLEX DYES		
Inochrome Orange RN	C.I. Acid Orange 72	Very good	6
Inochrome Blue 2J	C.I. Acid Blue 158 or 158A	Good	5
Inochrome Brown B2R (Fran)	—	Good	6
Inochrome Bordeaux RJ (Fran)	—	Good	6
Inochrome Black B	C.I. Acid Black 52	Good	6
	2:1 METAL-COMPLEX DYES		
Neutrichrome Yellow JRL (Fran)	—	Very good	7
Vialon Fast Yellow R	C.I. Acid Yellow 119	Very good	7
Neutrichrome Orange RL (Fran)	—	Very good	7
Neutrichrome Red JL (Fran)	—	Very good	7
Vialon Fast Red B	C.I. Acid Red 225	Very good	7
Neutrichrome Grey 6BL (Fran)	—	Very good	6
Neutrichrome Black RL (Fran)	—	Very good	7–8
Vialon Fast Black R	C.I. Acid Black 63	Very good	7–8
	COPPER-COMPLEX DIRECT DYES		
Diazol Light Brown BRN	C.I. Direct Brown 95	Very good	7
Diazol Light Brown 8RL	C.I. Direct Brown 112	Very good	7
Diazol Light Brown 2RL	C.I. Direct Brown 96	Very good	6
Diazol Light Blue 3JLN	C.I. Direct Blue 98	Very good	7
	DIRECT DYES		
Diazol Fast Yellow 2F	C.I. Direct Yellow 28	Good	6–7
Chrysophenine J extra conc.	C.I. Direct Yellow 12	Good	5
Diazol Orange BR	C.I. Direct Orange 20	Good	4
Diazol Brilliant Orange JN	C.I. Direct Orange 1	Good	4
Diazol Brilliant Orange 2RN	C.I. Direct Orange 1	Good	4
Diazol Brilliant Orange 2JN	C.I. Direct Orange 1	Good	4–5
Diazol Fast Orange S	C.I. Direct Orange 26	Good	4–5
Diazol Scarlet B	C.I. Direct Red 37	Good	4
Diazol Fast Scarlet 5BS	C.I. Direct Red 14	Good	5
Diazol Rose R	C.I. Direct Red 31	Good	3–4
Diazol Fast Red F extra	C.I. Direct Red 1	Good	6
Diazol Fast Bordeaux 3B	C.I. Direct Red 16	Good	4–5
Diazol Fast Bordeaux RS	C.I. Direct Red 88	Good	4–5
Diazol Brown M	C.I. Direct Brown 2	Good	4
Diazol Violet BS	C.I. Direct Violet 22	Good	3
Diazol Blue 3R	C.I. Direct Blue 3	Good	3
Diazol Pure Blue 6B	C.I. Direct Blue 1	Good	3
Diazol Green B (Fran)	—	Good	5
	COPPER PETHALOCYANINE		
Diazol Light Turquoise JL	C.I. Direct Blue 86	Very good	7–8
Alcian Blue 8GS (ICI)	—	Very good	7–8
Zapon Fast Blue HFL	C.I. Solvent Blue 25	Very good	7–8
	ACID DYES		
Acid Light Yellow 5R	C.I. Acid Orange 3	Good	6–7
Supracid Yellow 5JL	C.I. Acid Yellow 22	Good	6
Supracid Yellow R	C.I. Acid Yellow 25	Good	6
Milling Yellow 7JL	C.I. Acid Yellow 44	Good	4–5
Milling Yellow 3J	C.I. Acid Yellow 42	Good	5–6
Pyrazolone Yellow 3J double	C.I. Acid Yellow 37	Good	6–7
Orange II	C.I. Acid Orange 7	Good	4–5
Xylidine Orange L	C.I. Acid Orange 17	Good	3–4
Acid Light Orange J	C.I. Acid Orange 10	Good	4–5
Supracid Orange 3J	C.I. Acid Orange 35	Good	5
Milling Orange R	C.I. Acid Orange 79	Good	4–5
Milling Scarlet R	C.I. Acid Red 97	Good	4–5
Milling Scarlet 5B	C.I. Acid Red 89	Good	3
Acid Fast Red BRL	C.I. Acid Red 118	Good	5–6
Acid Fast Red 4BL	C.I. Acid Violet 14	Good	6
Supracid Red 2J	C.I. Acid Orange 19	Good	5–6
Supracid Red J	C.I. Acid Red 181	Good	5
Supracid Red 3B	C.I. Acid Red 35	Good	4–5

TABLE I—*continued*

Dye	*Colour Index* No.	Tinctorial Value	Light Fastness
Milling Red J	C.I. Acid Red 85	Good	5
Milling Red B	C.I. Acid Red 124	Good	4–5
Milling Red 3B	C.I. Acid Red 132	Good	4
Supracid Brown R	C.I. Acid Brown 35	Good	5
Supracid Brown 4R	C.I. Acid Brown 23	Good	6
Fast Acid Green BL	C.I. Acid Green 31	Good	5
Fast Acid Green B	C.I. Acid Green 19	Good	5
Alizarin Green J	C.I. Acid Green 25	Very good	7
Brilliant Alizarin Green B extra (IG)	—	Medium	6–7
Alizarin Cyanine Green 5G	C.I. Acid Green 41	Medium	6–7
Acid Alizarin Sky Blue B	C.I. Acid Blue 78	Very good	7
Acid Alizarin Sapphire SE	C.I. Acid Blue 43	Medium	6–7
Brilliant Fast Cyanine BL	C.I. Acid Blue 59	Good	6
Brilliant Fast Cyanine JL	C.I. Acid Blue 101	Good	6

Thus we had discovered a new method of dyeing, which, to our surprise, seems to be of wide practical interest, since it enables us to dye such acrylic polymers directly with numerous soluble and insoluble dyes at high temperatures and in presence of hydroxylamine or one of its salts.

The main purpose of the present paper is to outline the results of our study, for which a patent claim has been formulated.

To complete this general introduction, we may add that, apart from the cuprous-ion method, the use of hydroxylamine or its salts as assistants in the dyeing of acrylic fibres, first described in the Cassella patent [3] cited above, has been studied also by F. L. M. Schouteden [4–6]. This author showed that the acrylic polymer can be chemically modified by the action of hydroxylamine at a temperature of 75–100°C., and thus acquires an increased affinity for acid dyes.

E. Wagner [7] also has reported an increase in the affinity of acrylic fibres for dyes as a result of the action of hydroxylamine.

Finally, this principle has been applied by Pacific Mills [8] in a recent U.S. patent. The acrylic fibre is treated generally at the boil with a hydroxylamine salt, partially neutralised with alkali-metal hydroxide or carbonate, and then dyed at high temperature in acid medium.

II— Dyeing Method

1. PRINCIPLE OF THE METHOD

The fibre is dyed in a 10–20 : 1 liquor containing the dye and 1–10 g. of hydroxylamine sulphate per litre at 120–130°C. for 30–60 min. After dyeing, the fibre is rinsed, soaped at 50–60°C., rinsed again, and dried.

In order to show the general application of this procedure, we give in Table I some lists of dyes of different chemical classes which were applied to Orlon 42 (DuP) in presence of hydroxylamine sulphate, and indicate for each example an approximate tinctorial value as well as the corresponding light fastness for dyeings at 2% depth. Moreover, all these dyes have good fastness to washing and to hot-pleating. These lists of dyes are in no sense exhaustive, and many other brands can be applied by the procedure described above.

The 2 : 1 metal-complex dyes are of great practical interest, as they possess the following characteristics—

(*a*) They nearly all have some intrinsic affinity, low but not negligible, for acrylic fibres at high temperatures. The dye exhaustion is greatly increased in presence of small quantities of hydroxylamine sulphate: thus the bath is completely exhausted when only 1–4 g. of this product is added per litre.

(*b*) They have excellent light fastness.

TABLE II

Effect of Hydroxylamine on Exhaustion (%) of Dyebath

Temperature of dyeing		125°C.	125°C.	Boil
Presence of hydroxylamine		None	Sulphate	Hydrochloride
Neutrichrome Yellow JRL (Fran)	—	—	95	—
Vialon Fast Yellow R	C.I. Acid Yellow 119	30	95–100	—
Inochrome Orange RN	C.I. Acid Orange 72	0–5	90	10–20
Neutrichrome Orange RL (Fran)	—	30	95–100	—
Neutrichrome Red JL (Fran)	—	—	95	—
Vialon Fast Red B	C.I. Acid Red 225	30	95–100	45–55
Diazol Fast Scarlet 5BS	C.I. Direct Red 14	0–5	90	—
Acid Alizarin Sky Blue B	C.I. Acid Blue 78	0–5	90	—
Diazol Light Blue 3JLN	C.I. Direct Blue 98	0–5	95	10–20
Alizarin Green J	C.I. Acid Green 25	0–5	90	—
Neutrichrome Grey 6BL (Fran)	—	—	95	—
Neutrichrome Black RL (Fran)	—	—	95	—

2. EXHAUSTION

In order to get an idea of the true practical value of this method of dyeing, we have noted in Table II some numerical values of dye exhaustions after high-temperature dyeing in the presence and in the absence of hydroxylamine, as well as at 100°C. in presence of hydroxylamine.

(*a*) DYEING AT HIGH TEMPERATURE— The details are given in § 1.

(*b*) DYEING AT 100°C.— The 250:1 liquor is set with, per litre—

8·4 g. ... Hydroxylamine hydrochloride
6·0 g. ... Anhydrous sodium carbonate
0·08 g. ... Dye

The fibre (Orlon 42) is dyed at the boil for 25 min.; 8 c.c. of glacial acetic acid is then added per litre of dyebath, and dyeing is continued at the boil for a further 30 min. The fibre is then rinsed, soaped at 50–60°C., rinsed again, and dried.

It can be concluded from these results that—

(*a*) The 2:1 metal-complex dyes have a certain affinity for the acrylic fibre at high temperatures, and that affinity is greatly increased by addition of hydroxylamine sulphate to the bath

(*b*) Acid and direct dyes dye the acrylic fibre only in presence of hydroxylamine sulphate

(*c*) Exhaustion is greatly improved at high temperatures.

Of course, these results vary according to the nature and the origin of the acrylic fibre, e.g. Crylor (Rhodiacéta), Orlon 81 (DuP), Pan (CFM), Dralon (FBy).

3. COLOUR RANGE; SHADING AND LEVELLING

Most of the dyes examined gave dyeings which, naturally, were not as bright as those given by basic dyes. This is hardly surprising, especially in the case of the metal-complex dyes, which are known to be dull.

Nevertheless, we obtained bordeaux, browns, navy blues, bottle greens, greys, and blacks in heavy depths, even with combinations of dyes of different chemical classes. For instance, the following recipe gives a beautiful grey—

0·15% Neutrichrome Yellow JRL (Fran) —
0·15% Vialon Fast Red B (C.I. Acid Red 225)
0·70% Acid Alizarin Sky Blue B (C.I. Acid Blue 78)

Good, level dyeings are obtained, and there is no difficulty in shading during dyeing.

4. DYEING OF FIBRE MIXTURES

Unions of cellulosic and acrylic fibres can be dyed as follows: the acrylic fibre is dyed first at 120–130°C. in presence of hydroxylamine sulphate, preferably with acid or metal-complex dyes (since direct dyes would dye the cellulosic fibre preferentially). The cellulosic fibre is barely stained, and may be cross-dyed by normal dyeing methods, below 100°C., with direct or vat dyes according to the fastness required.

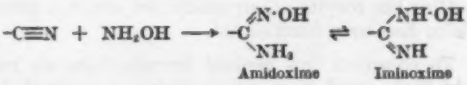
For wool–acrylic fibre unions this method of dyeing at high temperature is unsuitable, because wool cannot be treated above 105°C. without damage. At that temperature the acrylic fibre does not possess sufficient affinity for dyes even in the presence of hydroxylamine. Only the 2:1 metal-complex dyes would be suitable, but they would dye the wool preferentially.

5. TENSILE STRENGTH

The decrease in tensile strength of Orlon 42 yarns dyed by the high-temperature method described above is about 12–14% compared with the untreated yarn. This loss is of about the same order as that of yarns dyed at 115°C. with basic dyes (11–13%).

III— Theoretical

It is well known in organic chemistry [9] that hydroxylamine adds on to the nitrile group to form an amidoxime—



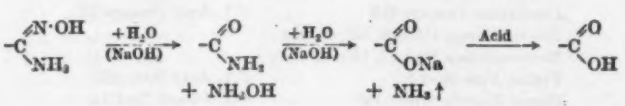
An amidoxime contains two reactive groups— amino and hydroxyl— which enable it to chelate with metals such as iron, copper, and nickel, since they are linked to the same carbon atom. Thus the possibility of the formation of an amidoxime grouping in the acrylic polymer when it is treated with hydroxylamine may explain its affinity for the dyes mentioned above.

CHEMICAL CONSTITUTION OF THE ACRYLIC FIBRE AFTER TREATMENT WITH HYDROXYLAMINE

Yarns of Orlon 42 have been treated with different quantities of hydroxylamine sulphate at different temperatures, and the following analyses made— (*a*) quantitative estimation of the amidoxime or any other easily hydrolysable grouping; (*b*) elementary analysis for nitrogen, oxygen, carbon, and hydrogen.

(*a*) *Estimation of Amidoxime, etc.*

The fibre is treated with a 2% caustic soda solution at 95–100°C., excess of alkali eliminated, the fibre acidified, and the excess of acid titrated. The principle of the determination is shown by the following scheme—



Formation of ammonia is actually observed during the hydrolysis.

The fibre (0·1 g.) is introduced into a test-tube, 10 c.c. of 2% caustic soda solution added, and the

tube heated at 95–100°C. on a boiling water-bath for 3 hr. The fibre is filtered off on a sintered-glass Gooch crucible, thoroughly rinsed with hot water until excess alkali is removed, and placed in a 250-c.c. conical flask; 20 c.c. of water and 10–20 c.c. of 0·1 N. sulphuric acid are added with stirring, and the flask is allowed to stand for 5–10 min.

The fibre is again filtered off on a sintered-glass Gooch crucible, and rinsed with a few c.c. of water to remove excess acidity. The filtrate and washings are then titrated with 0·1 N. caustic soda, when the quantity of acid which has disappeared corresponds to the number of carboxyl groups formed by hydrolysis, or in other words, to the number of amidoxime or other easily hydrolysed groups present in the fibre.

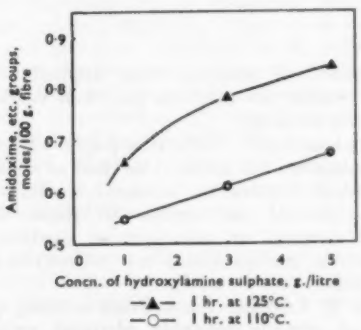


FIG. 1— Effect of Conditions of Treatment on Proportion of Amidoxime, etc. Groups in Treated Fibre

The results are plotted in Fig. 1. A blank experiment (no hydroxylamine in the bath) gave a negligible result (0–20 m-moles/100 g.). These curves show clearly that it is better to operate at temperatures well above the boil, i.e. at 125°C.

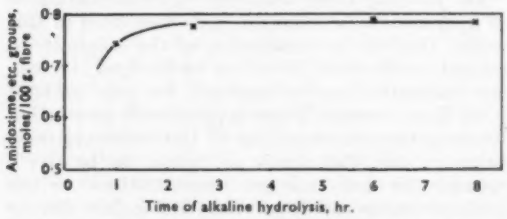


FIG. 2— Effect of Time of Alkaline Hydrolysis on the Number of Amidoxime, etc. Groups

An indication of the accuracy of this method of estimation is given by Fig. 2, which shows that after 2½ hr. of alkaline hydrolysis there is no appreciable further increase in the number of amidoxime, etc. groups. It appears that the nitrile groups are not hydrolysed by the 2% caustic soda solution, and thus do not interfere in the analysis; this is also confirmed by the result of the blank test.

(*b*) *Elementary Analysis*

The results of the quantitative elementary analysis of certain samples are grouped in Table III.

TABLE III

Elementary Analysis of Treated Orlon 42

Treatment			N	O	C	H
Hydroxylamine Sulphate (g./litre)	Temp. (°C.)	Time (hr.)	(%)	(%)	(%)	(%)
0	—	0	24·17	0·7	66·38	6·0
5	110	1	23·65	2·35	65·60	6·17
5	125	1	23·33	3·24	64·88	6·66

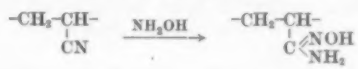
In comparison with the untreated Orlon 42 fibre, we observe—

(i) A slight decrease in the amounts of nitrogen and carbon

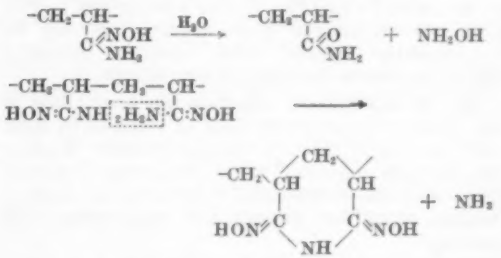
(ii) A slight increase in the amount of hydrogen

(iii) An appreciable increase in the proportion of oxygen, or, more precisely, the appearance of oxygen in the polymer.

The changes in carbon, hydrogen, and oxygen are readily explained by the reaction between the nitrile group and hydroxylamine sulphate to produce an amidoxime grouping—



The decrease in the nitrogen content, instead of an increase, cannot be well understood unless secondary reactions are supposed to take place, such as—



The first reaction is a hydrolytic process and takes place only in aqueous medium, while the second proceeds more probably in anhydrous medium.

F. L. M. Schouteden [4] showed by infrared examination that there is no possibility of hydrolysis, since amide and carboxylic groups are absent, and suggests the internal cyclisation shown by the second equation above. This is quite logical, since this author was studying the reaction between polyacrylonitrile and hydroxylamine in a solvent medium, viz. dimethylformamide.

But in our case, as the reaction has been carried out in aqueous medium, the hypothesis of the hydrolysis of the amidoxime into amide should rather be retained, since we operate at 125°C. and the final pH of the reacting solution is about 2–3. Moreover, the presence of such amide groups would explain equally well the small but appreciable decrease in the percentage of nitrogen, the appearance of oxygen in the polymer, and the different changes in the percentages of carbon and hydrogen.

IV— Conclusion

The results which are presented in this paper show the interest of the new method of dyeing acrylic fibres at high temperature in presence of hydroxylamine or its salts. We are at present carrying on further studies to determine more exactly the nature of the reactions which take place and consequently to explain the dyeing of these fibres.

We would like to express our thanks to the management of the Compagnie Française des Matières Colorantes for permission to publish this paper, and to our colleagues for assistance during this work.

COMPAGNIE FRANÇAISE DES MATIÈRES COLORANTES
LABORATOIRE D'APPLICATION DE L'USINE DE
VILLERS SAINT-PAUL (OISE)
FRANCE

(*MS. received 7th May 1957*)

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Discussion

Mr. E. STEAD: Is the reduction in tendency to accumulate a static electrical charge accompanied by an alteration in hydrophilic properties?

M. KHACHOYAN: It must be, since an increased affinity of the soluble anionic dyes for the treated fibre is observed.

Mr. A. MURRAY: Has this dyeing process any effect on the handle of Orlon 42?

M. KHACHOYAN: Dyeing at these elevated temperatures causes a shrinkage of the fibre, because of its plastic character, and consequently a change in its handle. But in view of the hydrophilic character the fibre acquires, it can be subsequently treated with suitable softening agents to restore the original soft handle.

Mr. B. KRAMRISCH: Mention has been made in the paper of a good standard of fastness to light and washing of most of the dyes tested. What is the position regarding other properties of special interest to the woollen and worsted trades, such as fastness to sulphur stoving, acid cross-dyeing, and potting?

M. KHACHOYAN: The fastness to acid cross-dyeing and potting is not as good as that to light and to washing. Unfortunately, the fastness to sulphur stoving has not been examined.

Mr. J. RANKIN: Have the authors any information on fastness to permanent pleating?

M. KHACHOYAN: We mentioned in the paper that fastness to hot-pleating is very good, as the dyes we have used are not disperse dyes and consequently do not sublime.

Mr. RANKIN: Has any work been carried out using this method for the pack-dyeing of loose fibre or slubbing? I should have thought that at these elevated temperatures the density of the pack would be such that the penetration of the dye liquor would be completely prevented.

M. KHACHOYAN: We have not yet applied our method to the pack-dyeing of loose fibre or slubbing.

Dr. W. L. LEAD: It is stated that infrared examination has shown that both amide and carboxylic groups are absent in the case of the product formed in non-aqueous medium. Has this method of analysis been applied to your product where the reaction has been carried out in aqueous medium?

M. KHACHOYAN: Since this paper was written we have applied the infrared method of analysis to the product treated in aqueous medium. The results obtained are similar to those for the product formed in non-aqueous medium [4]: in other words, neither amide nor carboxylic groups are present.

Dr. G. H. LISTER: Since Orlon is being sold by virtue of certain desirable physical properties, can it be claimed that, after the hydroxylamine treatment, the fibre is still Orlon, with the same physical properties?

M. KHACHOYAN: The most desirable physical property of Orlon is probably its handle, which can be restored, after the hydroxylamine treatment, by means of suitable softening agents, and the fibre is still Orlon.

Dr. LISTER: Comparatively high concentrations of hydroxylamine sulphate have been used in this work. Can the concentration of the sulphate be related to the depth of colour to be dyed; i.e. can low concentrations be employed for pale colours?

M. KHACHOYAN: There is practically no relation between the concentration of the hydroxylamine sulphate and the depth of colour to be dyed, because for pale colours concentrations of the hydroxylamine salt lower than 1–3 g./litre (liquor ratio 20 : 1) will not give good results. This method is more economical for heavy dyeings.

Dr. L. VALENTINE: On the extent of reaction with hydroxylamine sulphate, there seems to be a discrepancy between two sets of data in the paper. In Fig. 1, values of 0·8 mole of amidoxime group per 100 g. of fibre are plotted; from the experimental method, however, the maximum amount of hydroxylamine present in the bath is 10 g. per 100 g. of fibre, equivalent to about 0·08 mole per 100 g. or 0·04 mole per acrylonitrile unit, i.e. only one-tenth of the number of amidoxime or other hydrolysable groups that are apparently introduced.

This suggests that acid hydrolysis of the polymer may play some part. Have blank experiments

been done to ascertain the effect of heating Orlon at 125°c. under the pH conditions obtaining in the treatment with hydroxylamine sulphate? It is possible that pretreatment under acid conditions increases the tendency to hydrolysis under the alkaline conditions of analysis. It is certain that the amount of hydroxylamine is insufficient to cause 40% transformation into ring structures of the type suggested.

M. KHACHOYAN: No blank experiments have been done under the pH conditions of the normal hydroxylamine treatment. We thank you for your suggestion, and will carry out further experiments to ascertain the effect of the acid conditions on the fibre in such a blank test.

The discrepancy between the experimental and the calculated values of the amidoxime or easily hydrolysed groups can be explained by the fact that the oxime functions, either present in an amidoxime group or attached to an imide ring, will liberate hydroxylamine base on acid hydrolysis, and this will react further with new nitrile functions. Nevertheless, this point needs clarification, and will be studied later.

Mr. W. H. HINDLE: Does the hydroxylamine treatment in any way affect the wrinkle-resisting or wrinkle-recovery properties of the acrylic fibre?

M. KHACHOYAN: We have not examined this particular point, and we do not know in what way this treatment affects the wrinkle properties of the fibre.

Mr. G. B. ANGUS: Does the proposed new method of dyeing have any effect on the soiling characteristics of the fibre; in particular, does it reduce the tendency to soiling?

M. KHACHOYAN: We have not made any measurements on the soiling properties, but we think that the tendency to soiling would be reduced, since the tendency of the treated fibre to accumulate electrostatic charge decreases, these two properties being closely related.

Mr. R. J. HANNAY: Is the use of hydroxylamine essential to the reaction described in this paper or can the changes in the acrylic fibre indicated in the theoretical discussion be brought about by the use of other reagents? The question is prompted by the knowledge that one of the main objections to the use of hydroxylamine or its salts in the cuprous ion method of dyeing is the toxic hazard to operatives, and the fairly high concentrations of hydroxylamine indicated in this paper would certainly cause a potential user of the process to question the toxic hazard involved.

M. KHACHOYAN: The chemical modification of the acrylic fibre does occur only with hydroxylamine. Many other reagents, mainly reducing agents, have been tried, but in no case has any affinity for anionic dyes been observed.

Mr. D. BLACKBURN: Can the hydroxylamine be applied as a pretreatment, and the dyeing carried out at a later, separate stage?

M. KHACHOYAN: The acrylic fibre can be pretreated with hydroxylamine sulphate and then dyed separately, but these two stages should preferably be carried out at elevated temperatures, in order to obtain good yields.

Mr. BLACKBURN: If the treatment is carried out on yarn or fabric, does any shrinkage of the material occur?

M. KHACHOYAN: Shrinkage of the material, whether yarn or fabric, does indeed occur.

Mr. J. B. SMITH: Did you observe any discoloration or degradation of the fibre, using the concentration of hydroxylamine sulphate used in the normal dyeing, or using only the hydroxylamine itself?

M. KHACHOYAN: Only a pale yellow coloration of the fibre is observed.

Mr. D. A. DOWNEY: The authors postulated a possible mechanism for the reaction between hydroxylamine and a polyacrylic fibre which involved the formation of a cyclic imine from the reaction of one molecule of the former with two adjacent nitrile groups on the latter. There would appear to be an equal probability of the bridging of two suitably adjacent chains via their nitrile substituents, and a corresponding modification of the physical properties of the fibre resulting from such cross-linking would be expected. Can the authors give any information on the increase in the degree of cross-linking on hydroxylamine treatment?

M. KHACHOYAN: The only information we can give you is the insolubility of the hydroxylamine-treated fibre even in hot dimethylformamide. The fibre swells and becomes disaggregated, but it keeps its fibrillar appearance.

Mr. E. E. BOWKER*: With cellulosic blends, the authors suggest dyeing the acrylic fibre first and then cross-dyeing the cellulosic fibre. What is the effect on the physical properties of the cellulosic fibre of the high-temperature treatment in the presence of hydroxylamine, and does this treatment have any effect on the dyeing properties of the cellulose?

M. KHACHOYAN*: A certain loss of tensile strength of the cellulosic fibre has been observed. This is mainly due to the final acid pH of the bath. No change is noted in the dyeing properties of the cellulosic fibre.

* Communicated.

Some Aspects of the Dyeing of Acrylic Fibres, with particular reference to the Pack-dyeing of Courtelle

K. MELDRUM and J. S. WARD

The general features of the dyeing behaviour and thermoplastic properties of acrylic fibres are discussed in relation to practical dyeing operations, in particular the pack- and package-dyeing of Courtelle in the form of loose fibre and slubbing. General and specific procedures for the application of disperse and basic dyes, consistent with the retention of good condition of the material, are suggested.

Introduction

A large number of acrylic fibres are today being made from polymers prepared by the process of addition polymerisation, using acrylonitrile as the principal monomer. This polymerisation process permits a wide variety of modifying components (co-monomers) to be combined with the acrylonitrile in many different ways. Consequently, with a wide choice of polymer composition and type available and the possibility of additional variety according to the method of conversion into fibre, almost every one of the acrylic fibres now being produced has a unique combination of properties.

The selection of a particular polymer composition or combination of properties by a fibre manufacturer will be based on a variety of grounds, discussion of which is beyond the scope of this paper. However, it is apparent both from the literature and from descriptive statements issued by fibre manufacturers, that considerable attention has been paid to securing adequate dyeability of acrylic fibres. This objective has been approached in several different ways, e.g.—

(1) Increase in the number or availability of the acidic groups present, so as to secure adequate dyeability with basic dyes

(2) Introduction of basic groups, so as to secure dyeability with acid, metal-complex, and mordant dyes

(3) Modification of the polymer structure so as to improve the light fastness of the dyed fibre, particularly with respect to disperse dyes

(4) Increase in the openness of the fibre structure so as to allow dyes (e.g. vat dyes, direct dyes) of larger molecular size than the average acid, mordant, or basic dyes to be used.

In consequence, the dyeing behaviour of many present-day acrylic fibres represents a considerable advance on that of earlier types. It is too early yet to say which of these several approaches offers the greatest advantage. A particular advantage of the last three approaches is that large ranges of dyes are already available from which to select individual dyes or combinations with appropriate dyeing behaviour and/or fastness. The success of the first approach has depended essentially on the ability of dyemakers to extend the range of basic dyes to include dyes of considerably higher fastness to light than those originally available; considerable progress has been made towards this end.

Dyeability of Courtelle

GENERAL

The manufacture of Courtelle* is based upon a polymer containing acidic groups in sufficient quantity to ensure good build-up of all basic dyes; saturation of the fibre with dye is virtually impossible under practical dyeing conditions. The conditions of fibre manufacture have been so adjusted that at normal dyeing temperature (i.e. just below the boil) the acidic groups are readily available to the dye, with the result that rates of dyeing are relatively high compared with other acrylic fibres.

Courtelle is therefore readily dyeable with basic dyes, and experience has shown that by using combinations of both the older and newer members of this range, relatively high fastnesses are attainable. Moreover, the basic dyes can with advantage in certain colours be augmented with the disperse dyes, which although not building-up so readily as the basic dyes, show to advantage in pale and medium depths where high light-fastness and ease of level-dyeing are of importance.

EFFECT OF TEMPERATURE

The effect of temperature on the absorption of basic dyes by Courtelle is illustrated in Fig. 1, in which the dye uptakes of two typical dyes in—

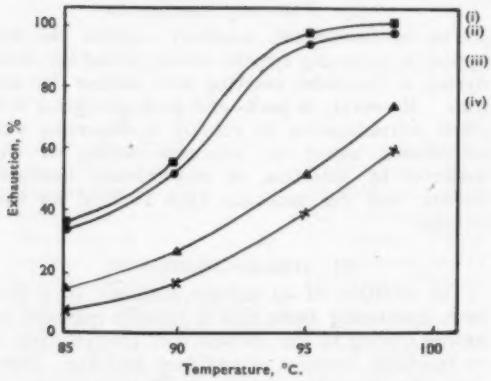
(i) Medium depths dyed for 1 hr.

(ii) Very heavy depths dyed for 2 hr.

are compared over the range 85–100°C.

It is obvious from these results that the uptake of basic dyes by Courtelle is very sensitive to temperature in this region. In this respect it is behaving similarly to other acrylic fibres. A particularly important feature of the present case is that the uptake at temperatures attainable in an open dyeing vessel is sufficient to allow heavy dyeings to be obtained in dyeing times of the order of 2–3 hr. even with a liquor ratio as high as 50 : 1.

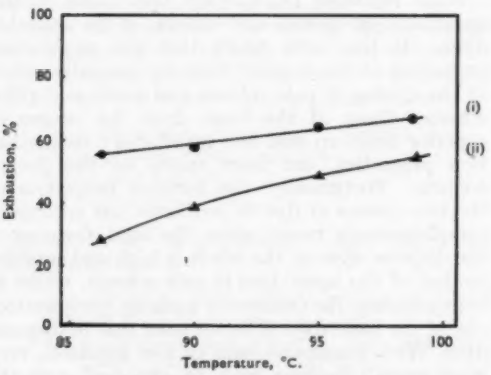
* *Courtelle* is the registered trade mark usedby Courtaulds Ltd. to designate their acrylic yarns and staple fibres.



(i) —■— 1% Methylene Blue 2B 150 (C.I. Basic Blue 9) for 1 hr.
(ii) —●— 1% Sevron Orange L (DuP) for 1 hr.
(iii) —▲— 4% Methylene Blue 2B 150 (C.I. Basic Blue 9) for 2 hr.
(iv) —×— 8% Sevron Red L (DuP) for 2 hr.

FIG. 1— Effect of Temperature on the Uptake of Basic Dyes by Courtelle (50:1 liquor at pH 5)

It is obviously advantageous, particularly with heavy depths, to apply basic dyes at the highest possible temperature, but care should be taken in the interests of level dyeing to approach maximum rate of absorption gradually, by control of temperature.



(i) —●— 1% Dispersol Fast Orange G 300 (C.I. Disperse Orange 3)
(ii) —▲— 1% Duranol Blue GN (ICI)

FIG. 2— Effect of Temperature on the Uptake of Disperse Dyes by Courtelle (50-vol. liquor containing Lissapol C (1:1000) for 1 hr.)

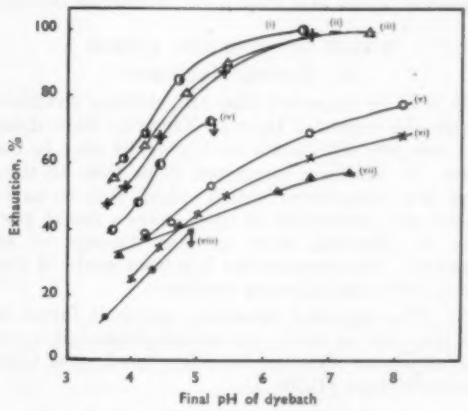
The absorption of disperse dyes in normal dyeing times is far less sensitive to temperature. This is illustrated in Fig. 2, from which it may also be seen that the extent of absorption over the whole range of temperatures is generally low, which, again, is typical of this type of dye on acrylic fibres.

From the point of view of application, the disperse dyes are therefore more suited to the dyeing of pale and medium depths, in which the low level of absorption is of little economic consequence, and, moreover, materially assists level application. With the more rapid-dyeing members of the range, absorption of dye at a useful rate occurs at 60–70°C., and at temperatures close to the boil appreciable migration takes place, allowing irregular dyeings to be corrected.

It should be appreciated, of course, that the above effects also operate in reverse, those dyes which can be applied at the lowest temperature also being most readily removed during subsequent scouring, laundering, and steaming operations. In spite of this, the disperse dyes as a class have remarkably good fastness to washing (e.g. Mechanical Washing Test A).

EFFECT OF pH

Since the dyeing of Courtelle with basic dyes consists essentially in the interaction of a weak acid and a weak base, the dye uptake should be influenced by dyebath pH. This is in fact found to be the case, and



(i) —◑— 1% Brilliant Green Y crystals (C.I. Basic Green 1)
(ii) —+— 6% Sevron Brilliant Red 4G (C.I. Basic Red 14)
(iii) —△— 6% Sevron Blue B (C.I. Basic Blue 21)
(iv) —◐— 4% Chrysoidine YN 160 (C.I. Basic Orange 2)
(v) —○— 6% Sevron Red L (DuP)
(vi) —×— 6% Sevron Orange L (DuP)
(vii) —▲— 4% Methylene Blue 2B 150 (C.I. Basic Blue 9)
(viii) —●— 3% Brilliant Green Y crystals (C.I. Basic Green 1)
↓ Precipitation

FIG. 3— Effect of pH on the Uptake of Basic Dyes by Courtelle (3-denier dyed in 50 vol. at 95°C. for 2 hr.)

Fig. 3 shows the results of a laboratory investigation of this effect. Dyebath pH values less than 4 have a pronounced retarding effect, which can be useful as a means of control in the early stages of dyeing. Increase in pH with some dyes is of considerable value in promoting build-up, but with other dyes difficulties may arise owing to dye precipitation or destruction. The pH range 4–5 is the most satisfactory for dyeing generally and is readily attainable by using a mixture of acetic acid and sodium acetate. It is often advantageous to start dyeing in a bath containing only the dye and the acetic acid which has been used to dissolve it, the pH being 3–3·5, and upon reaching maximum dyeing temperature to increase the pH slowly by addition of sodium acetate to a final value of 5. With heavy depths containing a relatively high proportion of Sevron Red L or Sevron Orange L, the pH may be further increased to 6·5–7, using sodium acetate or disodium hydrogen phosphate to secure fuller utilisation of these dyes and to make certain of obtaining their true colours.

Thus, to summarise—

(i) In general, an increase in dyebath pH causes an increase in exhaustion.

(ii) Certain dyes are decomposed or precipitated at too high a pH; these include—

Sevron Yellow L (C.I. Basic Yellow 13)
Sevron Yellow R (C.I. Basic Yellow 12)
Sevron Green B (C.I. Basic Green 3)
Brilliant Green YN (C.I. Basic Green 1)
Chrysoidine YN (C.I. Basic Orange 2)
Maxilon Blue GL (Gy)

(iii) Below pH 5 certain dyes (e.g. Sevron Red L and Sevron Orange L) do not yield their full tinctorial value and may give anomalous colours.

EFFECT OF AUXILIARY AGENTS

(*a*) *Cationic Auxiliaries*

It is to be expected that the cationic auxiliary agents, by reason of their similarity to basic dyes, will compete with them for the acidic sites in the fibre. It has been suggested from time to time that this competitive action, which acts so as to retard the absorption of dye, serves a useful purpose in allowing more uniform dyeings to be obtained. An examination has been made of this effect, with the following results—

(i) The expected retarding action is found in the majority of cases, the extent depending upon the particular dye and auxiliary used, and their concentrations (Table I).

TABLE I

Effect of Cationic Retarding Agents

(Time (min.) to reach 90% dyebath exhaustion in a 40:1 liquor of pH 4·5 at 98°C.)

Addition (%)	Retarder DS (DuP)	Lissolamine A (ICI)	Fixanol P (ICI)
	(i) 2% Sevron Blue B (DuP)		
Nil	15	15	15
0·5	30	55	30
1·0	—	80	40
2·0	50	130	55
4·0	100	190	—
	(ii) 2% Sevron Red L (DuP)		
Nil	35	35	35
0·5	75	85	50
1·0	90	—	55
2·0	—	195	70

(ii) This retarding action can be of value in improving levelness of dyeing only if it operates uniformly throughout the mass of material. Strike–migration tests suggest that in pack- and package-dyeing it will be at least as difficult to secure uniformity of retarding action as it is to secure uniformity of dyeing in the absence of the auxiliary agent. It has not been found necessary to attempt the use of cationic auxiliaries in the pack-dyeing of Courtelle with basic dyes, since satisfactory levelness can be obtained by other means.

It is possible that in piece-dyeing the action of retarding agents may be of greater value.

(*b*) *Non-ionic Auxiliaries*

The non-ionogenic auxiliary agents do not appear to have any specific action during the basic dyeing of Courtelle, reacting with neither dye nor fibre. However, in pack- and package-dyeing it is often advantageous to employ a dispersing and solubilising agent to minimise soiling of the material by filtration of adventitious insoluble matter, and the non-ionic type is ideal for this purpose.

(*c*) *Anionic Auxiliaries*

The addition of an anionic auxiliary to a dyebath containing basic dye is usually regarded as unwise, owing to the likelihood of precipitation of an insoluble complex of auxiliary and dye. However, the recently announced IT (Gy) process is apparently based on the use of a combination of anionic and non-ionic auxiliaries acting jointly as retarding agents, with the object of improving uniformity of dyeing, particularly with the Maxilon (Gy) dyes.

With disperse dyes, non-ionic or anionic dispersing agents, used in the normal manner, are both satisfactory.

Selection of Dyes

GENERAL

Some reference has already been made to the application properties and fastness of the available dyes. It has been noted that the application properties of the disperse dyes are generally suited to the dyeing of pale colours and medium depths, whereas those of the basic dyes, by reason of superior build-up and less satisfactory redistribution properties, are more suited to the deeper colours. Fortunately, the fastness properties of the two classes of dye fit well into this scheme of complementary usage, since the light fastness of the disperse dyes on the whole is high and superior to that of the basic dyes in pale colours, whilst in heavy dyeings the fastness to washing, perspiration, etc. of the basic dyes is better than that of disperse dyes. With reasonable care in dye selection, very good overall fastness may be expected over the whole range of depths.

DISPERSE DYES

A wide range of dyes, all having good overall fastness, is available, from which a selection can be made on the grounds of particularly desirable dyeing or fastness properties. The dyes listed in Table II have been found outstanding in the properties indicated.

BASIC DYES

Greater care is necessary in the selection of basic dyes, particularly when good light fastness is desired. At present some degree of incompatibility in dyeing behaviour must be accepted as the price of high light fastness in certain mixtures of dyes. In particular, combinations of the Brilliant Green type of dye with certain oranges and reds which are necessary to obtain heavy browns, greens, and greys of high light fastness (ca. 5–6) must be dyed first

TABLE II

Outstanding Properties of Selected Disperse Dyes

Dye	*Colour Index* No.	Fastness		Dyeing Properties	
		Light (> 5)	Steaming (10 min. at 10 lb./sq.in.)	Migration	Build-up
Cibacet Yellow GBA	C.I. Disperse Yellow 3	×		×	
Serisol Fast Yellow GGL	C.I. Disperse Yellow 33	×	×		
Dispersol Fast Orange B	C.I. Disperse Yellow 13		×		
Setacyl Orange RE	C.I. Disperse Orange 3	×		×	×
Cibacet Orange 4R	C.I. Disperse Orange 8	×			×
Supracet Fast Scarlet G	C.I. Disperse Red 19		×		
Artisil Scarlet GFL	C.I. Disperse Red 43		×		×
Serisol Fast Red BGL (YDC)	—		×		
Serisol Fast Red NGGL (YDC)	—	×	×		
Duranol Red 2B	C.I. Disperse Red 15	×		×	×
Supracet Fast Pink 3B	C.I. Disperse Red 11	×	×		
Duranol Brilliant Violet BR	C.I. Disperse Violet 8	×	×		
Duranol Violet RN	C.I. Disperse Violet 14		×		
Artisil Direct Violet 2RP	C.I. Disperse Violet 1	×		×	×
Serisol Fast Blue BGL	C.I. Disperse Blue 27		×		
Serisol Fast Blue BRL	C.I. Disperse Blue 19	×	×		
Cibacet Sapphire Blue 4G	C.I. Disperse Blue 16	×	×	×	×
Duranol Blue GN (ICI)	—	×			
Setacyl Blue 2GS	C.I. Disperse Blue 1	×	×	×	×
Duranol Navy Blue BN (ICI)	—	×	×		×
Supracet Fast Blue Green B	C.I. Disperse Blue 7	×	×		

in an acetic-acid bath to exhaust the majority of the green, before the pH is increased to obtain satisfactory tinctorial value for the red and orange components. The dyeing cannot be conducted throughout at high pH without danger of precipitating the green component. An example of this type of combination is given below.

DARK BROWNS OF HIGH LIGHT FASTNESS (5–6)
Brilliant Green Y (C.I. Basic Green 1)
Sevron Red L (DuP)
Sevron Orange L (DuP)

Examples of combinations which are more compatible are—

DARK BLUES OF HIGH LIGHT FASTNESS (ca. 5–6)
Brilliant Green Y (C.I. Basic Green 1)
Sevron Brilliant Red 4G (C.I. Basic Red 14) or Deorlene Brilliant Red 3B (Ciba)

DARK BROWNS, GREENS, AND GREYS OF MODERATE LIGHT FASTNESS (ca. 4)
Brilliant Green Y (C.I. Basic Green 1)
Sevron Brilliant Red 4G (C.I. Basic Red 14) or Deorlene Brilliant Red 3B (Ciba) or Magenta PN (C.I. Basic Violet 14)
Sevron Yellow R (C.I. Basic Yellow 12) or Maxilon Yellow 3GL (Gy)

MODE SHADES (MEDIUM TANS, GREYS, ETC.) OF HIGH LIGHT FASTNESS (ca. 5–6)
Sevron Blue 2G (C.I. Basic Blue 22)
Sevron Orange L (DuP)
Sevron Red L (DuP) or Maxilon Red BL (Gy)

Other dyes of interest are—

Maxilon Blue GL (Gy) Deorlene Dark Blue R (Ciba)	(Heavy blues of high light fastness)
Acronol Sky Blue 3G (C.I. Basic Blue 4) Deorlene Blue 5G (Ciba)	(Greenish blues of moderate light fastness)

DYEING OF BLACKS

The most satisfactory blacks are obtained with basic dyes. Disperse diazo blacks coupled with 3-hydroxy-2-naphthoic acid (C.I. Developer 8) are unsatisfactory from several points of view.

With basic dyes there are several approaches—

(i) Malachite Green (C.I. Basic Green 4) with Sevron Orange L (DuP), Sevron Yellow R (C.I. Basic Yellow 12), and Sevron Brilliant Red 4G (C.I. Basic Red 14). This combination gives at 98°C. a good black of light fastness 6, but the cost is relatively high.

(ii) Methylene Blue 2B (C.I. Basic Blue 9) with Magenta PN (C.I. Basic Violet 14) and Bismarck Brown RLN (C.I. Basic Brown 4). This combination gives at 98°C. a good black of light fastness 4–5, and it is fairly cheap.

(iii) Deorlene Black 290 or 4956 (Ciba). These dyes give rather greyish blacks of light fastness 5–6 and 4–5 respectively at a moderate cost.

(iv) Methic Black G (ICI) is a prepared mixture of relatively inexpensive basic dyes. Good, slightly bluish blacks having moderate light fastness (4–5) can be obtained at 98°C.

None of these combinations contains dyes which are wholly compatible, and the shade of black obtained may depend to some extent on the pH of application. A pH in the region of 4–5 is usually satisfactory, except for the Deorlene Blacks which require more acid conditions.

Selection of the appropriate method should be made in terms of shade of black required, fastness, ease of application, and cost.

Thermoplastic Behaviour of Acrylic Fibres during Dyeing

The mechanical properties of wet acrylic fibres change rapidly with increase in temperature, particularly over the range 50–100°C. It is obviously

important to the dyer to appreciate the extent of this change and the effects it may produce.

As the temperature is raised the wet fibre becomes more plastic, and therefore more readily deformable under the influence of the relatively small forces encountered in dyeing processes. For instance, compressive forces may result in appreciable consolidation of a mass of loose fibres, whilst tensile forces can produce extensions of yarns, and bending forces may result in creased fabrics. These deformations are essentially permanent, although so far as the fibres themselves are concerned the change is quite reversible, fibre mechanical properties returning to normal on cooling.

We have studied this phenomenon, in relation to the behaviour of Courtelle in stock- and slubbing-dyeing, in two ways—

(i) Measurement of the compression of packs of fibre in a model pack-dyeing system under hot wet conditions

(ii) Actual pack-dyeing trials.

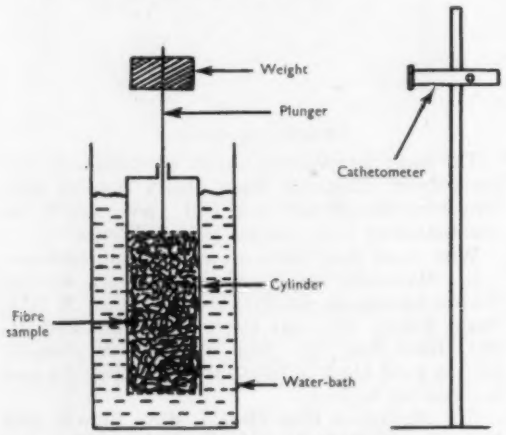


FIG. 4— Model System for Measurement of Compression of Packs of Fibre under Hot Wet Conditions

The apparatus used for the compression of packs of fibre is shown in Fig. 4. The cylinder is loaded with a fixed weight of fibre, which is wetted out with water at 40°C., compressed to give a package density of 17 lb./cu.ft., and allowed to come to equilibrium with the weighted plunger, the height of the pack being measured at this stage. The temperature of the water bath is raised rapidly to 60°C., and then raised in 10°C. steps to 100°C., the fibre being allowed to remain for 30 min. at each temperature, and the height of the pack being determined at 5-min. intervals. The type of curve obtained is shown in Fig. 5. It will be seen that, for each fixed load, the fibre pack tends to come to equilibrium with the load at a particular temperature. These "equilibrium" values for each of three different acrylic fibres under the same conditions of testing are shown in Fig. 6, and the effect of varying the load at a fixed temperature is shown in Fig. 7. The loads employed are similar to those which may be encountered owing to the pressure of circulating liquor in pack-dyeing machines.

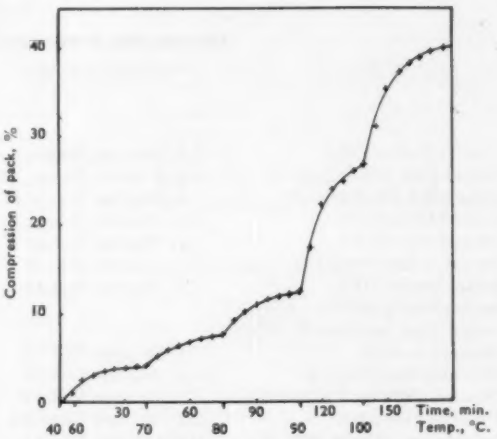


FIG. 5— Typical Compression–Temperature Graph (1·5-denier Courtelle under a fixed load equivalent to 3·3 lb./sq.in.)

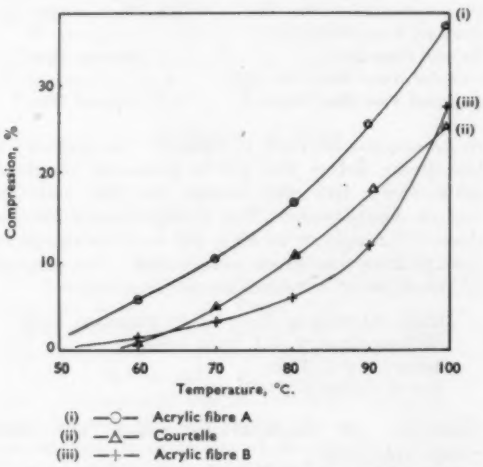


FIG. 6— Effect of Temperature on the Compression of a Pack (Model System) (applied load = 1·88 lb./sq.in.; all fibres 3 denier)

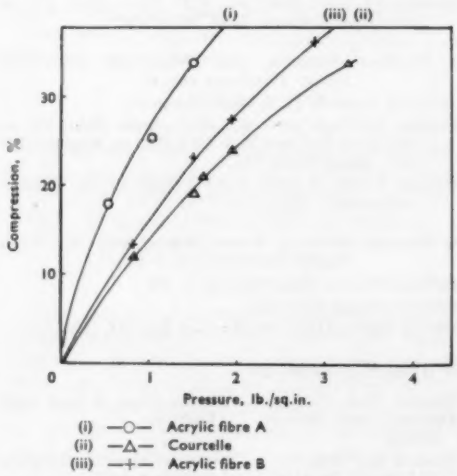


FIG. 7— Effect of Applied Pressure on the Compression of a Pack (Model System) at 100°C. (all fibres 3 denier)

It may be seen that—

(*a*) The extent of consolidation of a pack of acrylic fibre depends considerably upon both applied pressure and temperature.

(*b*) The extent of consolidation at the normal dyeing temperature of 90–100°C. can be quite large with relatively low values of applied pressure.

It should be noted that, although the plastic behaviour of the fibre is reversible in passing from cold to hot to cold, the consolidation effected whilst the fibre is plastic is essentially retained on removal of the pressure after cooling.

Pack-dyeing

It appears likely that Courtelle will require to be dyed in the form of—

(1) Loose stock for woollen spinning and for conversion into slivers used in the manufacture of knitted "fur" fabrics

(2) Slivers and slubbing for worsted spinning

(3) Tow for conversion into normal slubbing or for "turbo-stapling".

In each of these cases it will probably be dyed in pack- or package-dyeing machines. Our experience has shown that, under unsuitable dyeing conditions, two effects may occur—

(*a*) Collapse or deformation of the pack or package, with consequent channelling and unlevel dyeing

(*b*) Consolidation of the fibrous mass, leading to difficulties in further processing.

These effects both result from the thermoplastic behaviour of the fibre under the influence of the pressure of the circulating liquor, but they may be minimised by modification of machine operating conditions on the lines suggested by the laboratory investigation. For instance in the dyeing of loose stock, or slubbing in hank form in an Obermaier type of machine, the following modifications to procedure have been found advantageous—

(*i*) *Pack Stabilisation before starting dyeing*

This consists in hot, wet packing followed by high-temperature scouring, allowing the pack to be stabilised before dyeing is commenced.

(*ii*) *Liquor Circulation at Low Pump Pressure*

This consists in reducing the pressure at which liquor is circulated.

These modifications are carried out as follows—

Packing

Hanks of average weight about 2½ lb. could be packed dry in the cage to a density of about 10 lb./cu.ft., but the pack would fall considerably during liquor circulation at dyeing temperature. In the modified procedure, as each layer of hanks was put into the cage of the machine, water or scouring liquor at about 80°C. was poured over them, and the layer pressed down. By this means pack densities of about 17 lb./cu.ft. were readily obtained.

Scouring

In all subsequent processing it is advantageous to restrict liquor pressure across the pack to a maximum of 5 lb./sq.in. (for a 9-in. race) at the boil. In machines with high-efficiency pumps this may be achieved by throttling the inlet or outlet valves. Under these conditions the fibre was scoured with Lissapol N (ICI) and acetic acid (30%) (each at a concentration of 1 g./litre) at 95°C. for 30 min. The pack was well washed with cold water after scouring, and the lid screwed down to take up any gap. The pack densities after scouring were about 20 lb./cu.ft.

The high-temperature acidic scour is beneficial also in levelling out any differences in acid or alkaline reaction in the fibre, and thus bringing it to a constant and convenient pH before dyeing is begun.

It was found that by adopting this procedure the pack could be dyed at the open boil, using low pump pressures, without further sinking or channelling taking place, and that after dyeing the slubbing was still lofty after removal from the machine and shaking out the hanks.

It should be noted that the capacity of the machine was increased almost twofold by using the modified packing procedure.

CONTROL OF DYEING RATE

Basic Dyes

It is advisable in the interests of level-dyeing to exercise some control of the rate of absorption of dyes, particularly when dyeing the paler colours, so as to ensure initially level dyeing. This may be achieved by control of both temperature and pH. The possibilities have already been discussed, and a suggested procedure is given in Appendix A. Satisfactorily level results have been obtained consistently in bulk dyeings using this procedure with differential liquor pressures as low as 2 lb. per sq.in.

Disperse Dyes

Temperature control can also be used with advantage when applying these dyes, and with normal care level results are to be expected. A suggested general procedure for these dyes also is given in Appendix A.

Appendix B contains actual recipes and dyeing procedures used in specific cases.

Package Dyeing (Dyeing of Slubbing in Top Form)

It is also possible to dye Courtelle slubbing in package form, as the original ball or bump top. Two types of machine are normally used for this purpose, the can type and the spindle type.

Although it has been found possible to dye Courtelle tops in the can-dyeing machine, this procedure is not recommended. Very careful control of liquor pressure is required to prevent excessive consolidation of the tops, which, being densely packed in the first instance, offer considerable resistance to the flow of liquor. If can-dyeing should be attempted, the preliminary

scour should be at a low temperature, since pack stabilisation is unnecessary; pump pressure should not be higher than 2 lb./sq.in. throughout.

Courtelle ball-tops can be dyed successfully on the spindle-type machine, using a technique similar to that recommended for pack-dyeing. Hot, wet packing is unnecessary, but a high-temperature scour is advisable, after which the assembly should be checked and adjusted to give a satisfactorily close fit before commencing dyeing. It has not been found necessary to reduce pump pressure with this method of dyeing, presumably because the material is not being pressed against the outer wall of a dyeing vessel as in the other methods.

MATCHING

To facilitate matching and save time during dyeing, it is advisable when dyeing colours for the first time to prepare laboratory matchings, using the same liquor ratio as will be used in practice. This may be best achieved with one of the machines available commercially or described in the literature, but failing this, pot dyeings are satisfactory if carefully conducted. It is important to carry out this preliminary work at a temperature as close as possible to that at which the goods will be dyed.

SHADING

It will be necessary on occasion to make additions of dye for shading purposes after the normal dyeing period. In the case of disperse dyeings the temperature should be reduced to 80°C. or below before making additions. In the case of basic dyes, it may also be necessary to reduce the pH before making additions of dyes which are sensitive in the higher pH range, as well as reducing the dyebath temperature. Reduction of pH is best achieved by addition of hydrochloric or sulphuric acid, rather than acetic acid, since the bath is buffered.

Finishing of Dyed Material

After completion of dyeing, the material should be well rinsed with cold water, no special precautions being necessary, and checked for the presence of loose dye. This may be achieved by shaking a portion of the dyed material with cold methylated spirit for basic dyes, or cold acetone for disperse dyes. If the solvent is coloured, loose dye is present and may result in inferior fastness properties. In the case of basic dyes, loose dye is usually an indication of too high pH during dyeing, although with certain blacks it is difficult to avoid entirely. Loose disperse dye has usually been filtered out from an unsatisfactory dispersion, and should be avoided by selection of dye and dispersing agent on the basis of good filtration behaviour.

Correction of the material containing loose dye can usually be effected by an afterscour in a solution of detergent (preferably non-ionic and slightly acidified in the case of basic dyes). A special procedure for blacks is described in the Appendix.

Since the finish has been removed from the fibre during scouring and dyeing, it may be necessary to apply a finish after dyeing to ensure satisfactory processing.

The simplest method of finishing dyed slubbing is to treat cold with a cationic softener (e.g. 0·5% Alcamine (Allied Colloids) on weight of fibre), which in addition usually provides sufficient antistatic protection. If this finish should prove too soft or too slippery, the material should be impregnated with a non-ionic auxiliary (e.g. a 0·1% solution of Lubrol W (ICI) or similar product).

Loose fibre may require further antistatic protection, and proprietary products such as Brofostat E (Brown & Forth) applied by spraying 0·5% (on wt. of fibre) of the liquid with a hand spray to the hydroextracted material) are satisfactory for this purpose.

The material should be cold before hydroextraction, and since relatively little moisture is retained, low-temperature drying is quite satisfactory.

APPENDIX A

The Dyeing of Courtelle Slubbing

General Procedure— Pack-dyeing in Hank Form

Make up scour bath with—

Lissapol N (ICI) (or similar non-ionic detergent)	1:1000
Acetic acid (30%)	1:1000

at the boil.

Pack material into cage, wetting each layer with hot scour-bath liquor before adding more material.

Enter into scour-bath*, and treat at the boil for 30 min. Cool to 60°C. by addition of cold water. Drop scour-bath, and rinse with cold water.

Adjust lid of cage to accommodate any fall in level of pack.

Make up the dyebath as follows—

BASIC DYES— Paste the dye with the acetic acid. (For very heavy dyeings, e.g. blacks, the acetic acid is supplemented with an equal amount of methylated spirit.) Dissolve with water at 70–80°C., using a minimum of 3 gal. of water per lb. of dye, and strain into the dyebath containing dispersing agent.

DISPERSE DYES— Paste the dye with cold water. Disperse with water at 70–80°C., using a minimum of 3 gal. of water per lb. of dye, and strain into the dyebath containing dispersing agent.

Enter into the dyebath* at 60°C., and raise from 60°C. to the boil in 1 hr.

DISPERSE DYES— Continue at the boil as necessary. Cool bath to 80°C. before making any additions of dye.

BASIC DYES— Boil for 30 min., and then add sodium acetate crystals (1:1000) in portions during 1 hr. Continue at the boil as necessary. Cool to 80°C. before making any additions of dye.

After dyeing, cool the dyebath to 60°C. by adding cold water. Drop the dyebath. Rinse well with cold water before hydroextraction.

* To minimise consolidation of slubbing when scouring or dyeing at the boil, it is advisable to restrict the liquor pressure drop across the pack. This can be achieved by throttling the inlet or outlet valves until the difference in gauge reading is 5 lb./sq. in. or less (for a 9-in. race).

Aftertreatment of Heavy Dyeings (particularly Blacks)

A little surface dye, having poor wet fastness or rubbing fastness, is sometimes deposited when heavy depths are dyed. (Check by extracting a small sample with cold methylated spirit. If surface dye is present, bleeding into the spirit will occur.)

This should be removed by a clearing treatment with—

Formosul (C.I. Reducing Agent 2)	1:1000
Sodium dihydrogen phosphate (monosodium phosphate)	1:1000
Lissolamine A 50% paste (ICI)	0·5:1000

at 70°C. for 30 min.

Finish

If a soft finish is required, treat cold with 0·5% Alcamine (Allied Colloids) (or equivalent product) on weight of fibre, or with a cold 0·1% solution of Lubrol W (ICI).

APPENDIX B

(i) Blue on Courtelle Slubbing using Disperse Dyes

Packing

70 lb. of 3-denier 4-in. standard Courtelle slubbing was packed hot and wet, in hank form, into the cage of an Obermaier machine to a density of about 14 lb./cu.ft.

Scouring

The goods were scoured in 100 gal. (14 vol.) containing Lissapol N (1:1000) at 95°C. for 30 min., and rinsed with cold water. Pump pressure was about 5 lb./sq.in. Some sinkage occurred, and the lid was adjusted to give a tight pack— approx. 17 lb./cu.ft.

Dyeing

2% Duranol Navy Blue BN (ICI) and 0·2% Duranol Red X3B 300 (C.I. Disperse Red 11) were pasted with water, homogenised, and then added to the dyebath, previously set with Lissapol C (1:1000), at 40°C.

The goods were entered at 40°C., and the bath was raised to 95°C. over 60 min. and maintained at that temperature for 90 min. The material was then found to have been dyed to the required colour. The pack was rinsed by flooding with cold water.

Finishing

0·5% Alcamine (on wt. of fibre) was applied cold, and the material hydroextracted and dried in air.

This gave a pleasant blue of good washing fastness and light fastness 5 (Fade-Ometer).

(ii) Gold on Courtelle Slubbing using Basic Dyes

Packing

75 lb. of Courtelle slubbing, in hank form, was packed hot and wet into the cage of a Longclose dyeing machine to a density of 20 lb./cu.ft.

Scouring

The material was scoured with 120 gal. (16 vol.) containing Lissapol N (1:1000) and acetic acid (30%) (1:1000) at 98°C. for 30 min. Pump pressure was 4 lb./sq.in., and the direction of flow from the centre to the outside. No shrinkage occurred.

Dyeing

2·0% Sevron Orange L (DuP) and 0·63% Sevron Blue 2G (C.I. Basic Blue 22) were pasted with acetic acid (sufficient to give a concentration in the dyebath of 0·1% of 30% acid) and dissolved in hot water. The solution was added to the dyebath, previously set with Lissapol N (1:1000) and sodium acetate crystals (2:1000), at 60°C. The bath was now at pH 5·5, which was desirable in view of the fact that neither dye is sensitive to high pH, but Sevron Orange L gives an anomalous colour and poor exhaustion at pH below 5.

Dyeing was commenced at 60°C., and the temperature raised to 80°C. in 20 min. and to 98°C. in 60 min. After 2 hr. at this temperature the bath was nearly exhausted, and the colour was as desired.

Finishing

After rinsing, 0·5% Alcamine was applied cold, and the material hydroextracted and dried on frames.

The resulting gold dyeing has a light fastness of 5 (Fade-Ometer) and excellent fastness to dry cleaning, steaming, washing, and perspiration.

(iii) Dark Brown on Courtelle Slubbing using a Mixture of Basic Dyes having Poor Compatibility

Packing

30 lb. of 3-denier 4-in. standard Courtelle slubbing was packed hot and wet, in hank form, in the cage of an Obermaier machine to a density of approx. 14 lb./cu.ft.

Scouring

The material was scoured in 35 gal. (ca. 12 vol.) containing Lissapol N (1:1000) and acetic acid (30%) (1:1000) at 98°C. for 30 min., and then rinsed with cold water. Pump pressure was about 5 lb./sq.in. Some sinkage occurred, and the lid was screwed down to give a tight pack, of density about 18 lb./cu.ft.

Dyeing

The following dye mixture—

1·8% Sevron Red L (DuP)
0·8% Sevron Orange L (DuP)
0·4% Brilliant Green Y (C.I. Basic Green 1)

was pasted with 0·035 gal. of acetic acid (30%)— i.e. 1:1000— and dissolved in hot water. This was added to the bath previously set with Lissapol N (1:1000), at 60°C. (pH 3·8).

The goods were entered at 60°C., and the temperature was raised from 60° to 80°C. during 20 min., and then from 80° to 98°C. (open boil) during 50 min.

Sodium acetate solution was then drip-fed into the bath during 60 min. at the open boil to give a concentration in the dyebath of 0·1% sodium acetate (crystals) (pH 4·5). At this stage the green component, which is sensitive to pH > 5, was exhausted, and the bath contained some red and most of the orange.

Sodium acetate solution was again drip-fed during 60 min. to give a total concentration in the dyebath of 0·2% (pH 5·2). The bath was now practically exhausted. The pack was rinsed by flooding with cold water.

Finishing

A 0·1% solution of Lubrol W (ICI) was circulated cold, and the material hydroextracted and hung in air to dry.

This gave a heavy dark brown with the following fastness—

Light (Fade-Ometer)	5–6
Dry cleaning (trichloroethylene)	5
Mechanical Washing A	5
Perspiration	5
Steaming (10 min. at 10 lb./sq.in.)	5

(iv) Courtelle Combed Tops dyed on Spindle with Methic Black G (ICI)

Packing

The ball tops were dressed with cotton stockinet and placed on the (vertical) spindle of a Longclose dyeing machine.

Scouring

The material was scoured in 20 vol. containing Lissapol N (1:1000) and acetic acid (30%) (1:1000) at 98°c. for 30 min. and then rinsed with cold water. The differential pump pressure was ca. 10 lb./sq.in. cold, falling to 5 lb./sq.in. at 95°c., and the direction of flow was from centre to outside. Some consolidation took place, and the slack was taken up on the thread.

Dyeing

4% Methic Black G was pasted with sufficient acetic acid (30%) to make the dyebath concentration 0·1% with respect to acetic acid (30%), and dissolved in 40 times its weight of hot water. (N.B.— Methylated spirits may be used to supplement acetic acid to obtain a smooth paste.) This solution was filtered into the dyebath, previously set with Lubrol W (1:1000), at 60°c.

Dyeing was commenced at 60°c., and the temperature raised to 80°c. in 20 min. In the course of a further 60 min. the temperature was raised to the boil, and it was maintained there for 60 min. (pH 3·7).

Sodium acetate solution was run in during 30 min. to give a dyebath concentration of 0·1% sodium acetate (crystals) (pH 4·7), and dyeing continued at the boil for 60 min.

The pack was rinsed with cold water.

Afterscour

The material was found to be slightly bronzed (surface dye), and was therefore scoured at 60–70°c. for 30 min. in a bath containing—

Formosul (C.I. Reducing Agent 2)	1:1000
Sodium dihydrogen phosphate	1:1000
Lissolamine A 50% paste	0·5:1000

Finishing

After rinsing, 0·5% Alcamine was applied cold, and the tops were hydroextracted, and dried by passing them through a stove as used for viscose rayon cakes.

This gave a full black (slightly blue) of light fastness 4–5 (Fade-Ometer) and excellent fastness to dry cleaning, washing, and perspiration.

* * *

The authors are indebted to their colleagues, in particular Mr. D. Blackburn, of Droylsden Research Laboratory and Mr. R. Howard, of Droylsden Dyehouse, for their assistance, and wish to thank the Directors of Courtaulds Ltd. for permission to give this paper.

RESEARCH LABORATORY
COURTAULDS LTD.
DROYLSDEN
MANCHESTER

(MS. received 20th July 1957)

Discussion

Dr. J. F. GAUNT: During prescouring, use of Lissapol N and also of acetic acid at the boil are recommended. At this temperature it would be expected that the Lissapol N would come out of solution and filter out on to the surface of the pack. Has this been observed in practice? Also what is the function of the acetic acid, which is not normally used with Lissapol N for other fibres?

Mr. W. BEAL: Do the lecturers agree that the acetic acid used in the prescouring is necessary to stabilise the pH, and what substances do they intend to remove from the fibre with the Lissapol N used? Is this process really a prescour or a presour?

Mr. WARD: The object of the high-temperature prescouring process is threefold— (i) The high temperature assists in stabilising the pack before dyeing is started. (ii) The acetic acid stabilises the pH of the material at a constant and convenient level before dyeing with basic dyes is started. (iii) The Lissapol N assists in dispersing antistatic and other finishes present so as to provide a clean and constant substrate for dyeing. We prefer to use a non-ionic assistant for this purpose in view of the reactivity of anionic and cationic assistants towards basic dyes and Courtelle respectively. In view of the known high-temperature sensitivity of Lissapol N it may be that there is a more satisfactory assistant of this type, but in bulk dyeings to date we have experienced no difficulty in this respect.

Dr. GAUNT: Many forms of man-made fibre and particularly acrylics have a marked tendency to compact in a boiling dye liquor and thus make

penetration very difficult. It would be expected that the greater the thickness of material the greater the difficulty which would be encountered. Would the authors anticipate any particular trouble in dyeing in very large machines of, say, 500–600 lb. capacity?

Mr. WARD: It is clear from the work described that the results obtainable in the dyeing of Courtelle will differ considerably according to the type of machine being used. Although our experience has been confined to a maximum of 200 lb. per load, we should not expect to encounter any more difficulty when dyeing larger weights of tops in the spindle-type machine, or loose stock or hanked slubbing in the cage-type machine. Our experience with can-dyeing machines amply illustrates the difficulty which may be encountered in attempting to dye acrylic fibres under less suitable conditions.

Dr. GAUNT: The theory of the dyeing of acrylic fibres with basic dyes has received little attention in the literature, and there is virtually no published information on the structure of the special basic dyes or on that of the auxiliary products used with them. Different dyemakers recommend low pH and no retarder, or alternatively anionic retarders, cationic retarders, and non-ionic retarders, each under different pH conditions. Presumably all these methods refer to substantially the same class of dyes. I should be glad if the lecturers would comment on all this contradictory information in the light of their bulk experience.

Mr. WARD: Each of the methods of control mentioned by Dr. Gaunt has its counterpart in the dyeing of the basic fibres wool and nylon with acid dyes, and, as Dr. Gaunt is no doubt aware, the choice of method will depend upon prevailing circumstances, in particular the dyes being used and the type of material being dyed. We have stressed in our paper the individual behaviour of the basic dyes and mentioned certain difficulties due to poor compatibility. It may be that the use of one or other of the more specialised methods may assist with such problems, but our advice is—(*a*) examine these methods in the light of wool-dyeing experience; and (*b*) when dyeing loose stock, slubbing, or yarn, consider first the use of simple pH control, bearing in mind the optimum pH recommended by the dye manufacturers.

Mr. FRED SMITH: Acetic acid and formic acid are well known to retard the absorption of basic dyes, but certain dyes change colour at low pH. The original colour, we find, can be restored with cold solutions of ammonia. The red recommended for dyeing acrylic fibre used in a grey gives very bad colours in artificial light. Can the authors recommend a suitable orange of satisfactory light fastness that will obviate this?

Mr. K. MELDRUM: The most suitable combination of basic dyes recommended for the production of a grey of good fastness to light without any undue colour change in artificial light is—

Sevron Blue 2G (C.I. Basic Blue 22)
Sevron Orange L (DuP)
Sevron Red L (DuP

Under the recommended conditions of application, the initial pH of the dyebath will be approx. 4, which will assist level dyeing; and the final pH will be approx. 5, which will assist exhaustion and ensure that the true colours of the red and orange dyes are obtained.

Mr. G. S. MARR: Can the authors give an assurance now that the constitution of Courtelle will remain unchanged?

Mr. WARD: During the development of this fibre we have been at pains to collaborate with our colleagues from the manufacturing side on the many aspects of fibre production which can affect dyeing and finishing operations. The constitution of the fibre is only one of these aspects. However, we now believe that in Courtelle a combination of properties which is reasonably satisfactory to the dyer and finisher has been achieved, and we shall make every effort to ensure that the present standard is maintained.

Dr. D. PATTERSON: Many high polymers show transition temperatures below the melting point. Is the consolidation which occurs during dyeing associated with such a transition?

Mr. WARD: The consolidation of Courtelle which can occur during dyeing is caused by plastic deformation of the fibres, allowing them to become more closely packed. It will be seen from Fig. 5 and 6, which refer to the low-shrinkage fibre, that in the [illegible] condition there is a continuous increase in plasticity with increase in temperature and no indication of a discontinuity which could be attributed to a second-order transition.

Dr. PATTERSON: What is the melting range of the polymer?

Mr. WARD: This is of little interest technically and has not been determined.

Mr. B. KRAMRISCH: Could the lecturers give some information on the sighting of Courtelle, with respect to choice of dyes, method of application, and ease of subsequent removal?

Mr. WARD: Sighting colours (fugitive tints) for Courtelle should be chosen from the more water-soluble levelling acid dyes. The normal method of application is to spray a concentrated solution so as to tint the fibre without unduly wetting it. Greater care must be taken in the selection of dyes to ensure fugitivity when the material is to be heat-treated before wet processing, but otherwise on both normal and heat-treated material slightly alkaline soap or detergent scouring will ensure complete removal of the tint.

Mr. R. K. FOURNESS: In the studies on the application of disperse dyes in the package dyeing of Courtelle, were any limits set to the particle size of the dye to ensure levelness and to reduce to a minimum the need to remove loose dye after dyeing?

Mr. WARD: The level dyeing of Courtelle slubbing or loose stock with disperse dyes is not a particularly difficult matter, since exhaustions are relatively low and rates of dyeing may be readily controlled. In this sense, selection of dyes for level-dyeing behaviour on the basis of filtration properties does not appear as critical as in the case of cellulose acetate package dyeing, for instance.

The comments under "Finishing of Dyed Material" in our paper are concerned principally with the deposition of small amounts of loose dye on otherwise satisfactory dyeings and the prevention or removal of this so as to obtain the full benefit of the generally very good fastness properties of these dyes on Courtelle.

Mr. F. PARROTT: In the application to Courtelle of mixtures of dyes, e.g. of a dye which has to be applied at a low pH and one at a relatively high pH, what is the best procedure for shading?

Mr. WARD: An addition of the high-pH dye can safely be made after cooling the dyebath to 80°C. If the low-pH dye is to be added, the dyebath pH should also be reduced by addition of acid, and then slowly increased during the shading period.

Mr. FOURNESS*: In Appendix A you give details of the method of pasting up disperse dyes which is recommended by many dyemakers. These dyes occasionally pass through a sticky stage during this operation, which on the bucket scale can make the task a laborious one. This is due to the presence of the dispersing agent and has nothing to do with the melting point or other property of the dye itself. Because of this difficulty we have from time to time recommended a modified method of pasting which, we believe, eliminates the difficulty. This consists in reversing the normal procedure by sprinkling the dye powder into warm water (at about 60°C.) with good agitation.

Mr. WARD*: We have on occasion encountered this difficulty, but in our preoccupation with other matters have neglected to examine alternative methods of pasting. We are pleased to note this recommendation, which should be of value to many practical dyers.

* Communicated.

The Union Dyeing of Acrilan–Wool Blends

WALTER H. HINDLE

Early methods of dyeing Acrilan–wool blends in solid shades are outlined and the limitations stated. A new method is described which is applicable to all classes of wool dyes. Data are presented to show how the concentration of sulphuric acid and of a cation-active dyeing assistant may be varied to control the relative dyeing rates of wool and of Acrilan and the migration of dye from wool to the Acrilan acrylic fibre to produce solid shades.

Acrilan* consists of at least 85% acrylonitrile together with other comonomers designed to enable the fibre to be dyed with anionic dyes by conventional techniques. Other acrylic fibres are being, and have been, dyed with anionic dyes using the cuprous-ion principle. The latter system is not necessary in the dyeing of Acrilan, as weakly basic groups have been incorporated in the copolymer to allow anionic dyes to be applied by methods similar to those used in the dyeing of wool. The dyeing of Acrilan with anionic dyes differs from the dyeing of wool in that more acidic conditions are required to obtain maximum tinctorial yield and fibre penetration. With most wool-type dyes, sulphuric acid is necessary to effect full fibre penetration, although it is not necessary to bring about dyebath exhaustion.

Acrilan is highly resistant to both organic and inorganic acids. A treatment for 8 hr. at 95°C. in a 40% solution of sulphuric acid results in a loss in strength of less than 10%. From this, it is obvious that the dyeing of 100% Acrilan with wool-type dyes in the presence of sulphuric acid presents no problem from the standpoint of fibre degradation. Although 100% Acrilan may be dyed with a wide range of dyes other than those used for wool, in the dyeing of Acrilan–wool blends application of wool dyes is by far the simplest method.

A résumé of the progress made in the dyeing of Acrilan–wool blends with wool dyes will be a useful way to approach the data presented later in this paper. The first of these blends were dyed with the acid-dyeing metal-complex dyes in the presence of relatively high concentrations of sulphuric acid. Selected dyes from this group gave excellent solid colours with 8–12% sulphuric acid based on the weight of goods and a dyeing time of 3–6 hr. at the boil. In the early stages of the dyeing, the wool component of the blend absorbed by far the greater proportion of the dye, but on prolonged boiling the excess of dye was desorbed from the wool and subsequently absorbed by the Acrilan component to yield a solid result. The concentration of acid, although similar to that used with these dyes on wool, was considered to be excessively high. There were also limitations to the range of dyes suitable for application by this method: some of these dyes did not dye the Acrilan–wool blends solid, and in the light and medium blues the light fastness was so poor as to demand the use of other classes of dyes to complete the colour range. Further study revealed that a more positive transfer of dye from the wool to the Acrilan could be accomplished by a method which subsequently became known as the *cation-transfer method*.

Acrilan requires pH values below 3·0 to permit effective dyeing. Of course, these conditions are such as to increase the rate of dyeing on wool to a point where uniform results are almost impossible. At the lower pH values many neutral-dyeing wool dyes are precipitated and, in some cases, demetallised. It became obvious that a system would need to be developed whereby a wider range of dyes could be applied uniformly to the blend without incurring the rapid strike on the wool component. Investigations showed that a number of cation-active compounds were effective in promoting the level dyeing of wool. Studies on Acrilan–wool blends revealed a number of such compounds which would promote the transfer of dyes from wool to Acrilan in the presence of sulphuric acid. Because of this effect, it was possible to dye solid colours by first dyeing the wool conventionally and then effecting a transfer of the dye by addition of a cation-active substance and sulphuric acid. The quantities of sulphuric acid required to effect this transfer were considerably lower than those used in early work, the improved method taking 40% less acid than the previous method.

The range of dyes was still limited, but it had been considerably broadened, and now included selections from all classes of dyes employed in the colouring of wool with the exception of the neutral-dyeing metal-complex dyes. Although it has always been difficult even on 100% wool to obtain good light fastness in the paler colours, this method would not allow the use of these dyes, which have such good fastness to light on wool. The main reason for not employing these dyes is their inability to transfer once they have dyed the wool fibre. This, actually, is not too surprising in view of their behaviour on wool.

The position, then, facing the dyer with the cation-transfer system was that a relatively full

* *Acrilan* is the registered trademark for the acrylic fibre manufactured by The Chemstrand Corporation at Decatur, Alabama, U.S.A. A plant is at present under construction for the manufacture of Acrilan in the United Kingdom.

colour range could be dyed by a one-bath method giving good solidity between the Acrilan and the wool. In the pale colours, for which neutral-dyeing metal-complex types are employed on 100% wool, light fastness was lacking and dyeing time was longer than that used for dyeing wool itself. The concentrations of sulphuric acid employed, although well within the limits normally used for the application of acid-dyeing metal-complex dyes to wool, were considered by some authorities to be in excess of those permissible for sound wool processing.

The third method of dyeing Acrilan–wool unions, and one which has been used widely in the United Kingdom, entails acid pretreatment. Early work had shown that Acrilan, like wool, absorbs acid, which is not subsequently removed by rinsing with water alone. The important point is that the acid is needed on the fibre and not in the bath. We found that, if fibres were pretreated with acid and then rinsed off before dyeing, the Acrilan is left in a condition to accept dye from the start at a rate nearly equal to that of wool. The chances of rapid and unlevel dyeing on the acidified wool, or of precipitation of dye on the acidified fibres, were removed by the addition of a non-ionic dispersing agent. Under these conditions Acrilan absorbs more dye than does wool at low temperatures. Above 70°C. the dyeing rate of the wool increases sufficiently to bring the fibres into union.

By this means it became possible to shorten dyeing times as compared with the cation-transfer system, and to reduce substantially the time during which the wool component of the blend was in contact with the higher concentrations of sulphuric acid. For neutral-dyeing metal-complex dyes no more than 4% sulphuric acid was necessary in the 30-min. pretreatment period. This method showed significant improvements in the light fastness obtained on the blends, though it was still not quite as good as that produced on 100% wool by normal dyeing methods.

Recent developments have suggested an improved method for dyeing Acrilan–wool blends by the use of dye–cation complexes. A selected group of cation-active dyeing assistants have this property, one of which, designated *A-203*, has been used in the experiments described in this paper. The complex formed in this way can be dispersed by the addition of a non-ionic material, subsequently referred to as *X-67*. X-67 is a wax-like substance of low melting point, generally classified as a polyoxyethylene ether of a fatty alcohol. In practice it was found advisable to combine requisite quantities of the cationic A-203 and the non-ionic X-67 before adding the dye solution. This eliminated the necessity for redispersing the complex formed and gave a straightforward operation readily handled in the dyehouse.

Visual examination of a dyebath prepared in this manner reveals no precipitate or insoluble material, as one would expect in such circumstances. It is interesting that the dye–cation complex, unlike the dye itself, can be completely extracted from the aqueous phase by such organic solvents as nitromethane and chloroform. There is no doubt that a true dye–cation complex is formed, however, for complexes of this nature with direct dyes, when prepared by the method described, do not dye cellulosic fibres, but do readily dye nylon under acidic conditions. The precise physical condition of the colouring matter has not been adequately defined, although present research tends to favour the hypothesis that the dye is present in the form of a finely dispersed oil-in-water emulsion.

For the purpose of illustrating the mechanics of the dyeing of Acrilan–wool unions from dye–cation complexes, Fast Scarlet BA (C.I. Acid Red 66) was chosen. The reason for this choice is that this dye is normally applied to wool from a weakly acid bath. Under these conditions of application it was impossible to obtain a satisfactory colour balance between the Acrilan and the wool in an Acrilan–wool blend, and it was expected that the use of sulphuric acid would present problems of levelling owing to the low pH required in the Acrilan–wool dyeing process.

A study was made of the exhaustion rates of Fast Scarlet BA on 100% wool and on 100% Acrilan using the following dyebath conditions—

0·5% Fast Scarlet BA (C.I. Acid Red 66)
1·5% X-67
4·0% Sulphuric acid

The dyeings were started at 25°C., and the temperature of the dyebath was raised to 100°C. during 30 min. at a rate of 2·5°C./min. The rate of dye absorption was determined spectrophotometrically.

Acrilan absorbs dye more rapidly than does wool at 25°C. (Fig. 1), but, as the temperature is raised, the dyeing rate for wool becomes much greater than that for Acrilan. At 70°C. wool has completely exhausted the dyebath, whereas for Acrilan equilibrium exhaustion is not reached until the temperature of the dyebath has reached 100°C.

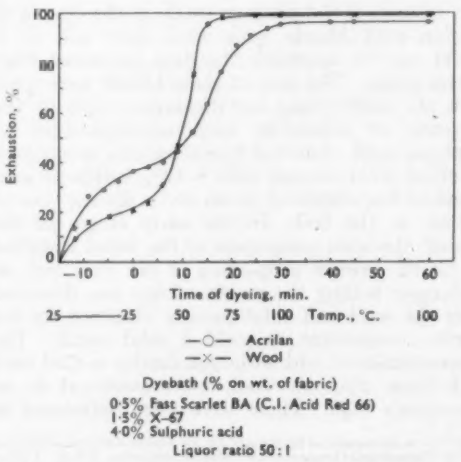


FIG. 1— Exhaustion Rate Curves for Acrilan and Wool

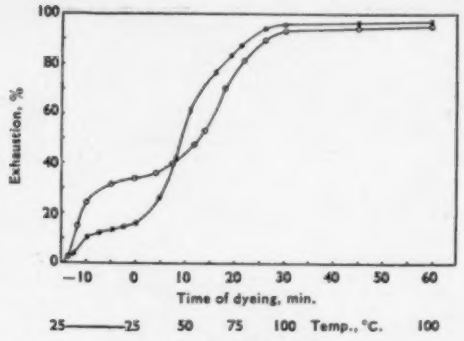


FIG. 2— 0·75% A–203

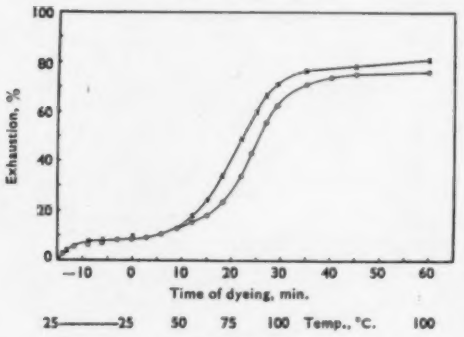


FIG. 3— 3% A–203

—○— Acrilan
—×— Wool
0·5% Fast Scarlet BA (C.I. Acid Red 66)
1·5% Triton X–67
0·75% A–203
4·00% Sulphuric acid
Liquor ratio 50 : 1

FIG. 2 and 3— Effect of A–203 on Exhaustion Rate Curves of Acrilan and Wool

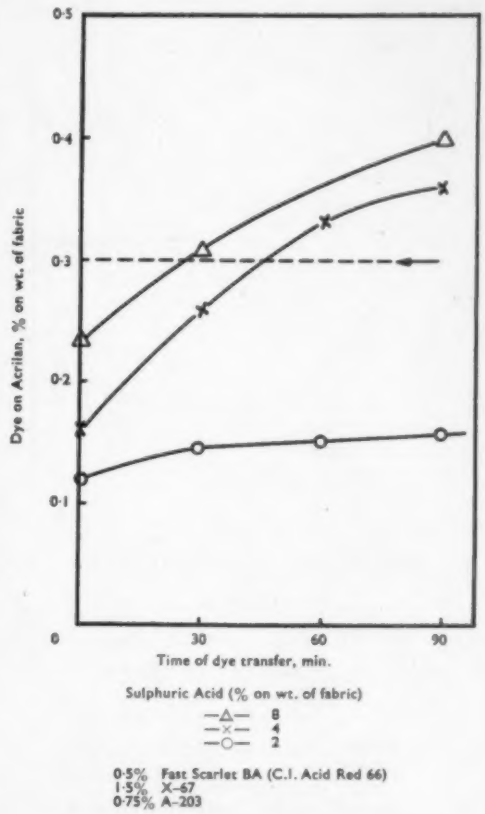

Dye on Acrilan, % on wt. of fabric
Time of dye transfer, min.
Sulphuric Acid (% on wt. of fabric)
—△— 8
—×— 4
—○— 2
0·5% Fast Scarlet BA (C.I. Acid Red 66)
1·5% X–67
0·75% A–203

FIG. 4— Effect of Concentration of Sulphuric Acid on Dye Transfer at 100°c. in Presence of A–203

A second series of experiments were carried out using a method of application precisely the same as the first except that 0·75% of A-203 (on weight of fabric) was added to each dyebath. Fig. 2 shows that dyeing rates on both fibres have been reduced, but to greater extent on wool, so that the curves for the two fibres now resemble each other more closely.

A third series of experiments showed that addition of 3% A-203 brings the dyeing rates of the two fibres still closer together, especially in the early stages of dyeing (Fig. 3), in marked contrast to the previous experiments. Even after 15 min. at the boil, only 80% exhaustion was obtained, as compared with 95% exhaustion when 0·75% A-203 was used.

The effects of the A-203 additive having been determined, there remained the necessity of determining the effect of the concentration of sulphuric acid on the system.

In the fourth series of experiments the fabric was a 50:50 Acrilan–wool fibre blend, which was dyed in a 50:1 liquor with—

0·6% Fast Scarlet BA
1·5% X-67
0·75% A-203

Three sets of dyeings were made, with 2, 4, and 8% sulphuric acid respectively. The dyeings were carried out at 100°c. for 90 min.

An examination of the three curves in Fig. 4 shows that with 8% sulphuric acid solidity can be obtained in approx. 25 min. at the boil, but with 4% sulphuric acid 45 min. is required to bring about uniformity, whereas 2% acid will not give uniformity even after 90 min. boiling.

From these data it is obvious that, under the conditions outlined in the series of experiments, sulphuric acid concentration has a very real part to play in obtaining adequate uniformity.

Dyeings were made on two separate lots of 100% wool with—

0·5% Fast Scarlet BA
1·5% X-67

and sufficient ammonium sulphate to exhaust the bath completely. To one bath an addition of 0·75% A-203 was made. After exhaustion, 4·5% sulphuric acid was added, and dyeing continued for 1 hr. At the end of the dyeing, one-half of the dyed wool was removed and replaced with an equal amount of undyed Acrilan. Both dyebaths were then raised to the boil and boiled for 2 hr.

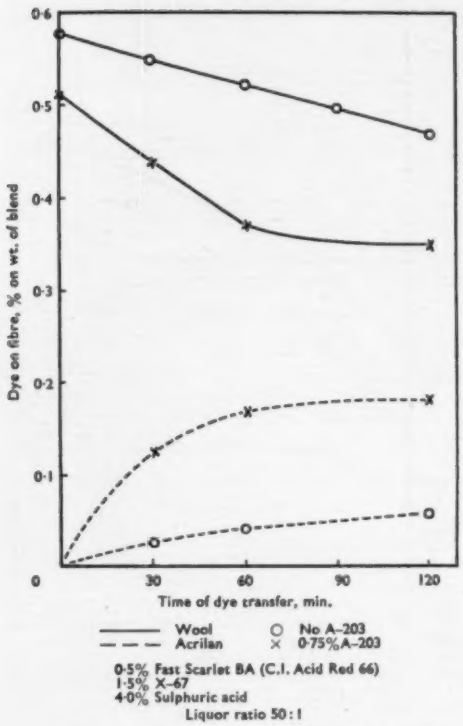


FIG. 5— Effect of A-203 on Dye Transfer at the Boil

Fig. 5 shows the relative distributions of dye on the two fibres. The transfer of dye from wool to Acrilan is seen to be more rapid in the presence of A-203. After 2 hr. boiling in the exhausted bath the wool dyeing containing the A-203 additive had lost 0·17% dye and the originally undyed Acrilan present in the same bath had picked up an equal amount to give a distribution ratio of 2:1 between the wool and the Acrilan. In the case of the wool dyeing without A-203, the wool lost 0·11% dye in 2 hr. and the Acrilan picked up approx. 0·06%, leaving the distribution ratio approx. 8:1.

To study the combined effect of sulphuric acid and A-203 on the union dyeing of Acrilan–wool blends a series of experiments was designed using a 50:50 blend dyed with—

0·5% Fast Scarlet BA
1·5% X-67

in which dyeing time and sulphuric acid and A-203 concentrations were varied. Four levels of each variable were employed, as follows—

(1) Sulphuric acid concentration (1, 2, 4, and 8%)
(2) A-203 concentration (0, 0·75, 1·5, and 3%)
(3) Time of dyeing at the boil (0, 30, 60, and 90 min.)

All possible combinations of these variables were employed, making a total of 64 separate experiments. At the conclusion of the dyeing operation, the colour balance between the Acrilan and the wool was determined both by reflectance measurements and by extracting the dye from the fibres.

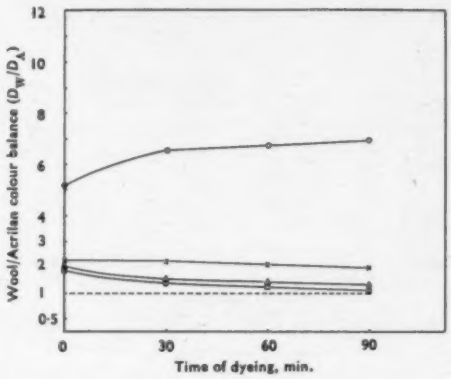


FIG. 6— No A-203

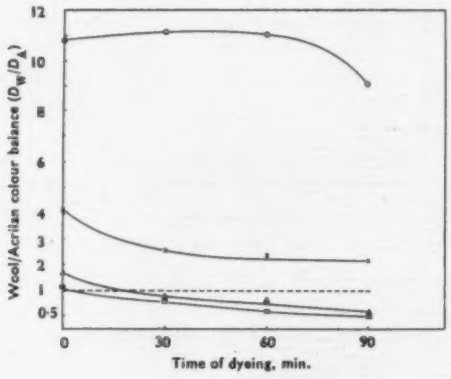


FIG. 7— 0·75% A-203

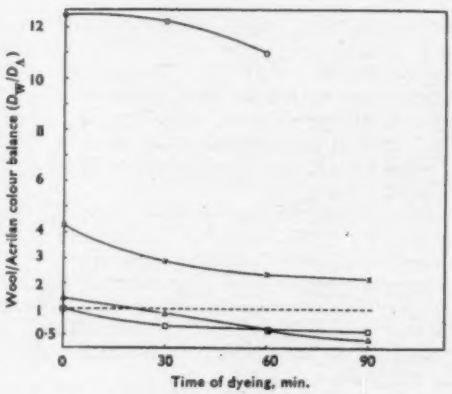


FIG. 8— 1·5% A-203

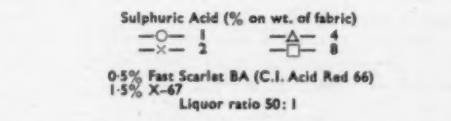


FIG. 6–12— Effects of Time of Dyeing and of Concentrations of Sulphuric Acid and A-203 on Wool–Acrilan Colour Balance at the Boil

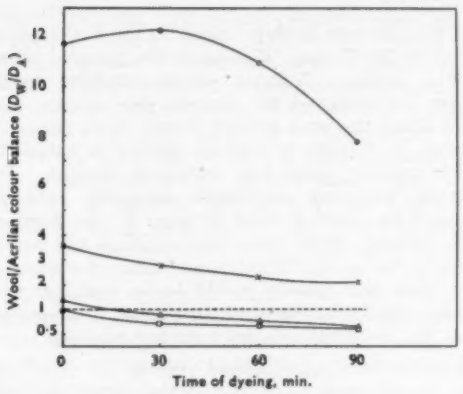


FIG. 9—3% A-203

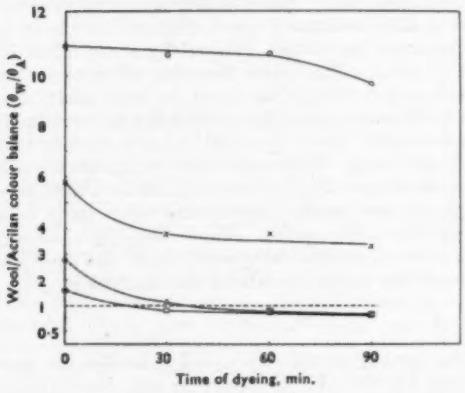


FIG. 10—0·75% A-203

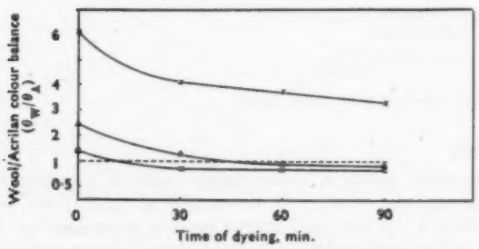


FIG. 11—1·5% A-203

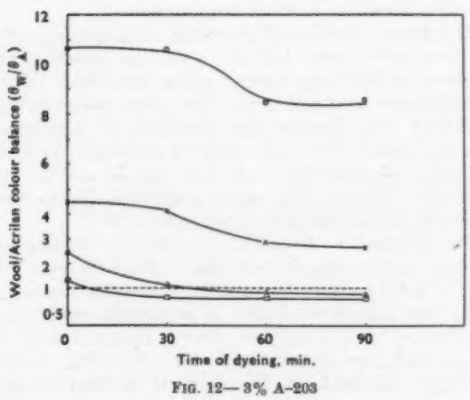


FIG. 12—3% A-203

Reflectance measurements R were converted to the Kubelka–Munk function—

$$\theta = \frac{(1-R)^2}{2R}$$

This function was found to be proportional to the amount of dye on the fibre. Extraction of the dye was accomplished with a 40:60 pyridine–water mixture. The wool–Acrilan balances for both methods are defined as follows—

$$\text{Wool–Acrilan balance (extraction)} = \frac{D_W}{D_A}$$

$$\text{Wool–Acrilan balance (reflectance)} = \frac{\theta_W}{\theta_A}$$

(D = % dye on fibre). The results are plotted in Fig. 6–12.

From these experiments the following conclusions were drawn—

1. At least in the case of neutral-dyeing acid dyes as represented by Fast Scarlet BA, the quantity of sulphuric acid used is critical in obtaining the union dyeing.

2. The retarding action of A-203 (which has been shown to retard the dyeing of wool more than that of Acrilan) is of material importance in attaining uniformity. The effect of A-203 is not a straight-line function of its concentration.

3. Time in relation to sulphuric acid and A-203 is another useful tool in controlling balance. For example, by using 8% sulphuric acid an over-balance of colour in favour of the Acrilan in a ratio of approx. 1·5:1 is obtained in 30 min., whereas when 4% sulphuric acid is used 1 hr. is required to obtain a similar ratio.

4. Not only can union dyeings be obtained from weak-acid dyes with the aid of sulphuric acid, but also, under different conditions, the Acrilan component of the blend can be dyed to a greater depth than the wool, giving tone-in-tone effects, as a result of the transfer effect illustrated by Fig. 5.

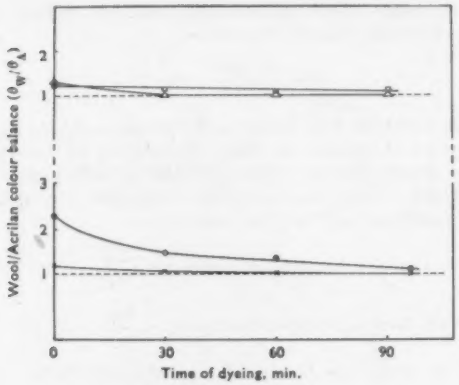
The next step is to review the information obtained in this investigation and to interpret it in terms of commercial practice in the dyeing of Acrilan–wool blends. The following conclusions seem justified in this connection—

A. The rate of dyeing of acid-type dyes from sulphuric acid baths can be controlled by the use of the systems mentioned.

B. Union dyeings can be achieved within dyeing times considered usual in the dyeing of 100% wool.

C. The quantity of sulphuric acid necessary to effect solidity has been reduced in comparison with previous methods. In the case of Fast Scarlet BA (C.I. Acid Red 66) 3% acid was considered to be the maximum requirement for a 60–90-min. dyeing cycle.

A number of dyes were evaluated for application in this way, and Fig. 13 illustrates the behaviour of dyes belonging to four classes—neutral-dyeing metal-complex, acid, acid metal-complex, and chrome dyes. As a generalisation, it was found that a very broad range of dyes could be selected



0·75% A–203
1·50% X–67
Liquor ratio 30 : 1

Dye	*Colour Index* No.	Sulphuric Acid (%)
—○— 2·0% Alizarine Light Blue SGL	C.I. Acid Blue 52	3·0
—×— 3·0% Gycolan Blue 2RL	C.I. Acid Blue 154	5·0
—△— 3·0% Acid Chrome Blue 3BA Conc.	C.I. Acid Red 12	5·0
—□— 1·0% Cibalan Blue BL	C.I. Acid Blue 168	2·5

FIG. 13— Union Dyeing of Wool–Acrilan with Various Classes of Dyes at the Boil

to give good fastness along with good uniformity. Neutral-dyeing metal-complex types generally require the least amount of sulphuric acid, usually of the order of 1–2·5% based on the weight of goods; chrome dyes and acid types require approx. 2·5–3·5%, with milling acid and acid metal-complex dyes requiring 3·5–5% sulphuric acid.

The method evolved from the experiments conducted is as follows— The previously prepared goods are allowed to circulate for 10 min. at 45°C., using a liquor ratio of 30 : 1. The following dyebath additions are made—

—	Dye
—	Sulphuric acid
0·75%	A-203
1·5%	X-67

The temperature is then raised to the boil over a period of 30–45 min. The goods are sampled after 45 min. boiling. Normal colour-matching techniques are followed for specific dye classes. In cases where the wool is more deeply dyed than the Acrilan, a further period of dyeing is allowed, which usually produces excellent unions. In isolated instances additional sulphuric acid is required to effect a solid dyeing. If the Acrilan were initially dyed more heavily than the wool, owing to the use of excessive quantities of sulphuric acid, then the remedy would be to wash off the dyeing and fill in the wool component in a second bath by conventional wool-dyeing methods.

Several hundred finished pieces of Acrilan–wool blends have been dyed by the above method based on the data presented here. The quality of dyeing uniformity, particularly with the neutral-dyeing metal-complex types, has been such as to prompt the use of this method by some dyers on 100% wool. The light fastness of dyeings on Acrilan–wool blends obtained by this method is markedly better than that obtained with previously recommended methods, and is now satisfactory for men's wear. This improvement has been made possible, in part, by the reduction in the amounts of sulphuric acid used. The dyeing times have been reduced to the point where they are closely similar to those for 100% wool, once the dyer has learned the salient points of the operation.

* * *

The author would like to acknowledge the part played by Dr. W. C. Carter in the development of this work.

CHEMSTRAND CORPORATION
DECATUR
ALABAMA
U.S.A.

(*MS. received 14th June 1957*)

Discussion

Dr. F. MANCHESTER: What are the conditions necessary for the reservation of wool in blends with Acrilan? Does the wool require a clearing treatment?

Mr. HINDLE: While it is a simple matter to reserve Acrilan in blends with wool, the reservation of wool is difficult owing to the staining characteristics of all classes of dyes on wool. Cationic and disperse dyes must be selected to give a minimum stain on wool. We have been successful in clearing the stain on wool by a combination of scouring and treatment with acidified sulphoxylate solutions.

Mr. W. BEAL: We find that it is more accurate to measure the concentration of acid in terms of grams or millilitres per litre rather than percentage on weight of fabric. Do you agree?

Mr. HINDLE: In order to obtain good colour balance between Acrilan and wool, the amount of sulphuric acid used, whether it be expressed on a solution basis or as a percentage on the weight of fabric, must be related to the liquor ratio. For example, when a lower liquor ratio is employed, the amount of acid (% on weight of fabric) can be reduced. If the acid concentration expressed on a solution basis is held constant as the liquor ratio is reduced, the wool component will be dyed more heavily than the Acrilan component.

Mr. BEAL: Less acid is needed with increasingly cationic assistants, but it is seldom possible to achieve satisfactory unions using less than 1·5 g. of sulphuric acid per litre. The more cationic the assistant the greater the amount of non-ionic product which has to be used to maintain the dye complex in solution, and this entails additional expense. Would you agree that this limits the strength of the cationic substance used?

Mr. HINDLE: Increasingly cationic assistants should require more, not less, sulphuric acid to obtain solid colours and good dyebath exhaustion. With the assistant A–203, a sulphuric acid concentration of 1·5 g./litre (40 : 1 liquor ratio) is considered the upper limit for obtaining union dyeings. Indeed, in the case of neutral-dyeing

metal-complex dyes, much smaller amounts are required, ~0·5 g./litre.

The amount of non-ionic product necessary for "solubilising" the dye complex depends to a great extent on the composition of the cationic assistant and not necessarily on its cationic strength.

Mr. H. R. HADFIELD: We have observed that the light fastness of certain acid dyes, when applied to Acrilan, increases as the amount of sulphuric acid is increased, e.g. from 3% to 8%. The improvement in light fastness can be as much as 2 grades. It is known that increasing the quantity of sulphuric acid over the amounts indicated above produces better penetration of the fibre by the dye. We understood the lecturer to say that the cationic agent suggested by him also produces better penetration of the fibre by the dye. Does the use of this agent likewise produce an improvement in light fastness with certain dyes?

Mr. HINDLE: We have always considered that light fastness is improved when the Acrilan fibre is well penetrated. This is true also for wool. Although the amount of sulphuric acid necessary for obtaining full fibre penetration is a function of each dye, it is not necessary to employ as much as 8% sulphuric acid (40 : 1 liquor ratio) to effect fibre penetration. We have no evidence to indicate that better fibre penetration results from using the cationic assistant A–203 or that light fastness is either improved or impaired by its use.

Mr. FRED SMITH: With reference to Mr. Hadfield's observations on the difference in light fastness, had the patterns been neutralised thoroughly before exposure?

Mr. H. W. PARTRIDGE: In view of the high wet fastness properties of anionic dyes on Acrilan, is any method available for stripping the dye from the Acrilan component of an Acrilan–wool blend?

Mr. HINDLE: Anionic dyes can be partly stripped from Acrilan by successive ammonia scours.

Mr. G. S. MARR: I am rather surprised to find Mr. Hindle taking pleasure in drawing specific attention to the dyeing differential between Acrilan and wool, because so often the inability to dye differing fibres in a mixed yarn to the same colour is regarded unfavourably, particularly as it disadvantageously reveals spinning irregularities.

Mr. HINDLE: The reason for drawing specific attention to the dyeing differential between Acrilan and wool is that, by proper choice of dyeing conditions, it is possible to obtain a variety of effects from solid colour through tone-in-tone effects to wool dyed–Acrilan reserved effects. In this paper, we have discussed only the dyeing of solid colours.

Mr. C. HOBDAY: Has the lecturer found any connection between the solubility of neutral-dyeing metal-complex dyes and their ability to form complexes with cationic agents? Indications are that dyes of low solubility complex more readily, and it should be possible to apply these dyes with less acid and get a satisfactory union between the wool and the Acrilan.

Mr. HINDLE: The amount of sulphuric acid required is not the same for all dyes, and appears to be related to the solubility of the dye, the least soluble dyes requiring the least acid. Dye mixtures must be selected for similar acid requirements.

Mr. H. BELLIS: Are A–203 and X–67 available to the trade in this country?

Mr. HINDLE: These products are available through Chemstrand Ltd.

The Dyeing of Acrilan and Wool–Acrilan Blends

G. H. LISTER

The acid-combining capacity of Acrilan has been determined using sulphuric acid at 60°C. The influence of pH on the dyeing of Acrilan with acid dyes has been examined, and the conditions required to obtain complete fibre penetration have been determined. The effect on the wool component of the blend and on the wearing properties of the cloths of the low pH required to dye Acrilan–wool blends satisfactorily with acid dyes has been investigated. The practical problems associated with the application of acid and chrome dyes in strongly acid dyebaths are discussed, and a dyeing method for their application is suggested.

Fibres of the acrylic group are finding increasing uses, both alone, in the knitwear trade, and in blends with wool, especially for materials to be given a durable pleat. The original acrylic fibres of the type of Orlon 42 (DuP) often require a lengthy or complex dyeing process, but the preparation of a copolymer of acrylonitrile and a product capable of conferring on the fibre an affinity for wool dyes appeared to offer a solution to dyeing difficulties, while still maintaining or improving upon the physical properties of the parent acrylic fibre. Products used as copolymers, and the manufacturers of acrylic fibres, have been listed by Kramrisch [1].

The material used in this investigation was Acrilan, provided by the Chemstrand Corporation, in the form of a sliver for tests on 100% Acrilan, and the same material with 64s-quality Botany slubbing for work on wool–Acrilan except where otherwise stated.

All materials were given a preliminary scour in a solution of a non-ionic detergent (2 g./litre) to remove oils and antistatic agents, dried, and conditioned.

THE DYEING OF ACRILAN

As a first step in determining the dyeing properties of Acrilan with acid dyes, the acid-combining capacity of the fibre was determined using sulphuric acid at 60°C.

The fibre was in contact with the acid liquors in a closed flask at 60°C. for 100 hr., tests having shown that this was sufficiently long to establish equilibrium between bath and fibre. The acid adsorbed was determined by titration of aliquots of the initial and final acid baths. The results are plotted in Fig. 1.

The basic groups of the copolymers are shown to be appreciably ionised only at pH values lower than 2·6, and at 60°C. the maximum acid-combining capacity is approximately equivalent to 2% sulphuric acid calculated on the weight of material.

The relation between the pH of the dyebath and the affinity of the fibre for acid dyes was next determined. Dyeings were carried out with four red dyes representing the level-dyeing acid type (Brilliant Sulphon Red B), the intermediate level-dyeing group (Xylene Fast Red P), and the milling type (Brilliant Alizarine Milling Red

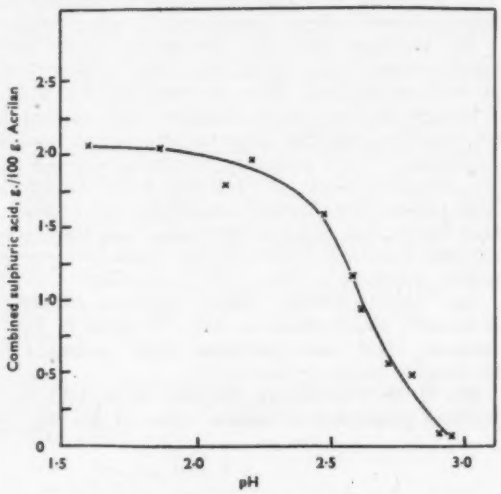


FIG. 1— Acid-combining Capacity of Acrilan at 60°C.

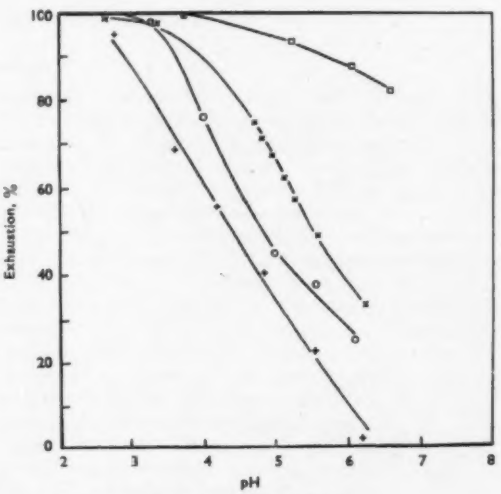


FIG. 2— Effect of pH on the Exhaustion of Selected Dyes on Acrilan

FBL), and a neutral-dyeing metal-complex dye (Lanasyn Red BL). The percentage exhaustion of the dyebath over a range of pH obtained with sulphuric acid, after boiling for 1 hr., was determined.

These results (Fig. 2) show that the neutral-dyeing metal-complex dye has good substantivity for the fibre in slightly acid dyebaths, and all the dyes examined gave satisfactory exhaustion at a pH of 3. Examination of cross-sections of all dyeings, however, showed that ring dyeing only had taken place. This was most marked with the milling dye and the neutral-dyeing metal-complex dye, but was present also with the level-dyeing and intermediate level-dyeing dyes. Since this indicates incomplete equilibrium, and at the same time will result in reduction in light and wet fastness, the factors influencing fibre penetration were more closely examined.

With the same four dyes in amounts equal to 5% calculated on the weight of material, tests were carried out, in the first instance keeping the pH constant and varying the time of boiling, and secondly varying the pH with a constant time of boiling. Results may be summarised as follows—

2% SULPHURIC ACID (pH 2·38)— All four dyes gave ring dyeings after 4 hr. boiling.

3% SULPHURIC ACID (pH 2·2)— Level-dyeing and intermediate level-dyeing acid dyes completely penetrated after 2 hr. boiling; milling and neutral-dyeing metal-complex dyes ring-dyed after 4 hr. boiling.

4% SULPHURIC ACID (pH 2·02)— Level- and intermediate-dyeing acid dyes penetrated after 1 hr. boiling; milling and neutral-dyeing metal-complex dyes required 3 hr. boiling for complete penetration.

Thus, although satisfactory exhaustion of a dyebath may be obtained under weakly acid conditions, to realise complete fibre penetration low pH values are required.

An examination of a wide range of acid dyes for fastness to light and wet treatments on Acrilan showed that the former property was in general unpredictable on the basis of the light fastness of the same dye on wool. The fastness to light is usually lower on Acrilan than on wool, but the neutral-dyeing metal-complex dyes have good light fastness, and a figure of 5–6, based on daylight exposure against the S.D.C. Blue Scale (*B.S.* 1006), is realisable with selected level-dyeing acid dyes. Wet fastness is normally equal to or slightly better than the wet fastness of the same dye on all-wool material, but the result is influenced by the degree of fibre penetration of the Acrilan.

Many acid and chrome dyes are precipitated at the pH values needed to get complete exhaustion of the dyebath and penetration of the Acrilan fibre. A dispersing agent is, therefore, required to prevent formation of tars and the filtering off of the precipitated dye acid. A non-ionic product of the type of Ekaline F was found to be the most suitable dispersing agent for this purpose.

The conditions of application of the chrome dyes to Acrilan are similar to those of the acid dyes; i.e. exhaustion may be obtained at a comparatively high pH, but more acid conditions are required to obtain fibre penetration. Development of chrome lakes, however, is more difficult on Acrilan than on wool, and larger amounts of dichromate are required with longer boiling times. The high dichromate content at the low pH sometimes gives rise to destruction of dyes which are sensitive to oxidising conditions, e.g. Omega Chrome Red B (C.I. Mordant Red 7).

For some purposes disperse dyes may be used on Acrilan, thus taking no advantage of the "wool-dyeing" properties of the fibre. The colouring power of a disperse dye on Acrilan is less than that of the same dye on secondary cellulose acetate. The general dyeing properties of the disperse dyes on acrylic fibres have been described by Kramrisch [1]. In general, little dyeing takes place below 60°c., and there is a large increase in rate of absorption at 70–90°c., necessitating careful temperature control in this region (Fig. 3).

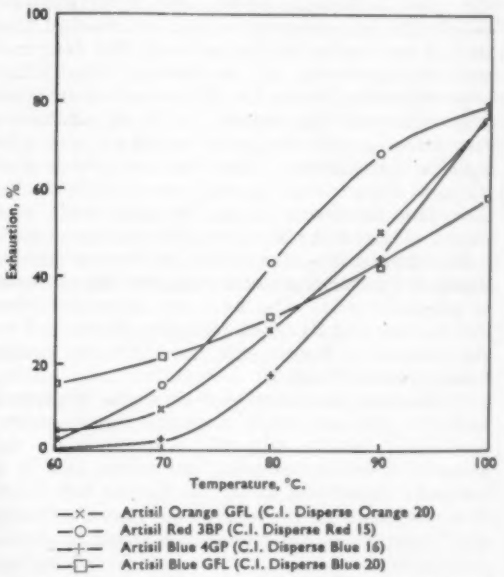


FIG. 3— Effect of Dyeing Temperature on the Exhaustion of Disperse Dyes on Acrilan

In pale colours the general fastness properties of the disperse dyes are adequate for most purposes, but the sublimation fastness of some necessitates careful dye selection if materials are to be given a durable pleating process.

THE DYEING OF WOOL–ACRILAN

If the affinity of Acrilan for acid and chrome dyes is utilised in the dyeing of blends of Acrilan with wool, the strongly acid conditions must be given special consideration because of the potential damage to the wool. In addition, the exhaustion of the acid or chrome dye on to the wool at the low pH values required for the dyeing of the Acrilan may be so rapid as to give rise to unlevel

TABLE I

Effect of Boiling Acrilan–Wool Blends with Sulphuric Acid on the Alkali Solubility of the Wool

Time of boiling	1 hr.		2 hr.		4 hr.	
Sulphuric Acid (%)	Final pH	Alkali Solubility (%)	Final pH	Alkali Solubility (%)	Final pH	Alkali Solubility (%)
2·0	3·76	13·7	3·7	13·0	3·66	17·2
4·0	2·92	15·7	2·95	19·2	2·99	27·4
6·0	2·46	20·5	2·55	28·3	2·59	43·4
8·0	2·27	23·1	2·32	36·5	2·33	60·0

dyeing on the wool portion, particularly with milling and neutral-dyeing metal-complex dyes.

Because of the higher acid-combining capacity of the wool, the amounts of acid required to give low equilibrium pH values in a union dyebath are much higher than when Acrilan alone is used. For example, on 100% Acrilan, 4% sulphuric acid calculated on the weight of material will give an equilibrium pH of 2; but on 50:50 wool–Acrilan material, 7% sulphuric acid is required to give the same pH; and with approx. 2·5% acid adsorbed by the Acrilan at the boil, the amount taken up by the wool is approx. 10·5% with a 20:1 liquor ratio. This is a quantity of acid in excess of that used in any normal dyeing process. The danger of acid damage to the wool is obvious. Since it has been established that a low pH is required to obtain penetration of the Acrilan, and an additional reason for strongly acid baths in union dyeing is to equalise the affinities of the wool and the Acrilan for acid dyes[2], experiments were carried out to determine the degree of acid damage to the wool that is obtained at pH values of the order required.

Equal quantities of wool and Acrilan were boiled together for varying times with varying amounts of sulphuric acid. The wool was separated from the Acrilan, and its alkali solubility determined by the method of Smith and Harris[3,4], the results being given in Table I.

Experience has shown that garments of all-wool material with an alkali solubility figure greater than 30 result in consumer complaints on the grounds of inferior wearing properties, and 25 is normally considered to be the highest safe limit. It is obvious from the above data that the dyeing conditions which are probably required to obtain satisfactory dyeing results on wool–Acrilan material are such that serious fibre damage to the wool might be anticipated. On the other hand, the presence of Acrilan in the blend might make it possible to accept a higher alkali solubility figure for the wool than would be possible with an all-wool cloth. This was next investigated.

Worsted cloth consisting of 50% wool and 50% Acrilan in the one case, and a cloth identical in weight and structure but composed of all wool, were subjected to the same treatment as the materials used in the previous test, and abrasion tests were carried out after conditioning for 24 hr. at 65% R.H. and 70°F., the tests being carried out under the same atmospheric conditions with a ring tester. The results are illustrated in Fig. 4 and 5.

The abrasion resistance of the wool–Acrilan cloth is initially higher than that of equivalent all-wool material. At the same time, the results

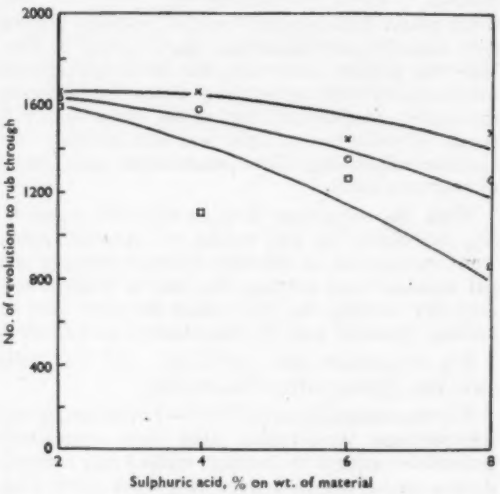


FIG. 4— Wool–Acrilan (50 : 50) Material

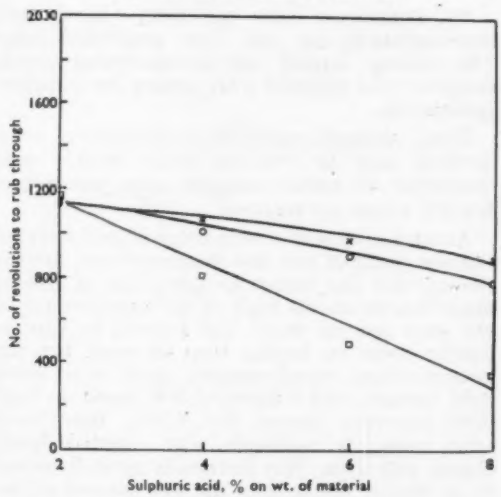


FIG. 5— All Wool

Time of Boiling
—×— 1 hr.
—○— 2 hr.
—□— 4 hr.

FIG. 4 and 5— Wearing Properties of Wool–Acrilan and All-wool Materials after Boiling with Sulphuric Acid

show that, if boiling is continued for longer than 2 hr. in the presence of more than 4% sulphuric acid (calculated on the weight of material), the decrease in resistance to abrasion is marked,

although the strength may still be only slightly less than that of the all-wool material in its original condition. The alkali-solubility figures (Table I), however, indicate that the wool component of the blend is damaged to an extent which would make it unacceptable in an all-wool cloth. Consideration of the ethics of using a treatment which gives this result is outside the scope of this paper. On the basis of the abrasion results, however, it can be decided that wool–Acrilan cloth, because of its initially higher resistance to abrasion and lower percentage decrease on being subjected to acid damage, compared with the behaviour of wool cloth, can be dyed under strongly acid conditions without undue risk of consumer complaints on the grounds of poor wearing properties.

An additional complication in considering the dyeing of wool–Acrilan material at low pH is the question of the properties of the acid or chrome dye on wool under such conditions. The rate of strike of all classes of acid and chrome dyes will be high and migration on the wool poor at the low pH, resulting in unlevel dyeing and poor rubbing fastness. It follows that the presence of an auxiliary agent which will retard the rate of strike on the wool is an essential from this point of view.

Two potential dyeing processes were first examined, both using level-dyeing acid dyes, to determine which gave the most satisfactory results assessed in terms of evenness of distribution of dye between wool and Acrilan.

In the first method the dye was applied to the fibres as it would normally be applied to an all-wool material. After obtaining satisfactory exhaustion of the dyebath, migration of dye from wool to Acrilan was promoted by reducing the pH of the dyebath with sulphuric acid, and at the same time a cationic product was added to assist removal of dye from the wool. This method ensures that the wool is dyed under conditions which give the optimum conditions for levelness.

In the second process an excess of a cationic agent was added to a strongly acid dyebath (pH 2·2) at the commencement of the dyeing. The purpose of this addition is to restrain the dyeing of the wool, especially at low temperature, when the affinity of the Acrilan for dye is lower than that of wool.

The advantage of this latter process is that it gives, at the commencement of dyeing, low pH conditions required for maximum affinity of dye on the Acrilan, and restrains uptake of dye by the wool until temperature conditions are also such that the affinities of wool and Acrilan are more nearly equal.

None of a wide range of acid dyes examined dyed Acrilan darker than wool at the end of the normal wool-dyeing process in the first method of application. Reduction of pH of the dyebath followed by a further period of boiling brought about transfer of dye from wool to Acrilan, and the addition of the cationic compound, while materially reducing the amount of dye on the wool, brought about only a slight increase in depth on the Acrilan. The effective result, however, was increased solidity, although a long boiling period was required to obtain a satisfactory result.

The second method of dyeing, using a low initial pH and a cationic restraining agent, brought about the same distribution of dye between wool and Acrilan as that obtained by the first method, but in an appreciably shorter dyeing time.

Examination of a range of cationic products showed little superiority of one over another as regards influence on distribution of dye between wool and Acrilan. The most effective method of increasing the amount of dye on the Acrilan is to decrease the pH of the dyebath. At the same time it must be stressed that a dyebath assistant is a necessity, firstly to obtain a level dyeing on the wool and secondly to prevent precipitation of dye acids or to keep them dispersed after precipitation. An auxiliary was prepared as a result of this work to give the most effective action in respect of both of these properties. It was a mixture of a cationic and a non-ionic product, termed *Lyogen WA*. Its effect on the light fastness of acid dyes was examined, and it was found that, in common with all cationic products, there was a slight decrease with some dyes, but this was insufficient to warrant a reclassification or alteration of the published data relating to their light fastness on wool.

For the ladies' dress goods and hosiery industries requiring bright colours of moderate fastness to light and wet treatments, level-dyeing acid dyes offer all that is required, and at the same time a simple method of dyeing which, with selected dyes, enables a solid result to be obtained on wool–Acrilan material in a dyeing time within the period beyond which acid damage to the wool becomes a serious factor.

The following dyeing method has been tried on many occasions and found to give satisfactory results on wool–Acrilan fabric. Quantities are expressed as percentages calculated on the total weight of material—

— Dye
5% Sulphuric acid
4% Lyogen WA

The dye is dissolved, the dyebath diluted, and the Lyogen WA added, followed by the sulphuric acid. The temperature of the dyebath is raised to the boil in 45 min., and boiling continued for 60 min.

Wool from bulk-dyed wool–Acrilan cloth dyed by this method was found to have alkali-solubility figures varying between 20% and 25% depending on the original quality of the wool, its early history, and the time required to obtain an exact matching of the required colour.

With a selected range of neutral-dyeing metal-complex dyes a slightly higher fastness to light and wet treatments may be obtained than with the best of the level-dyeing acid dyes. At the same time, solidity between wool and Acrilan can be obtained without resorting to such a low dyebath pH as is required by the level-dyeing acid dyes. Bright colours, however, cannot be obtained with this range. The most satisfactory dyeing

method is similar to the above, but the sulphuric acid is reduced to 3–4%.

The necessity for the presence of a cationic restraining agent and its use in relatively high concentration makes the effect of pH on the activity of the product of some importance, as is illustrated by the data of Table II.

TABLE II

Exhaustion of 1% Lanasyn Brown RL (C.I. Acid Brown 28)

Equilibrium pH	Exhaustion of Dyebath (%)
6·20	27·6
6·34	16·7
5·12	5·7
4·28	100·0
3·80	100·0
3·09	75·5
2·82	61·6
2·50	54·6

A 1% depth of Lanasyn Brown RL was dyed on 100% Acrilan sliver at the boil for 1 hr. over a range of pH values (obtained with sulphuric acid) in the presence of 4% Lyogen WA, exhaustion of the dyebath being determined colorimetrically at the end of that time.

The restraining action of the Lyogen WA appears to pass through a minimum. The reaction, however, is not a simple one and is being investigated further. The minimum-activity effect is most marked with the neutral-dyeing metal-complex dyes, and alternative explanations are possible.

The application of chrome dyes to wool–Acrilan materials is economically advantageous in dark colours. These dyes, however, require no special comment, since before chroming their reactions are similar to those of normal acid dyes. The presence of wool makes chrome lake development slightly easier than when such dyes are applied to 100% Acrilan.

* * *

Thanks are due to the Directors of Sandoz Products Ltd. for permission to publish this paper and to Mr. D. K. Clough for assistance in its preparation.

SANDOZ PRODUCTS LTD.
CANAL ROAD
BRADFORD 2
YORKSHIRE

(*MS. received 19th June 1957*)

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Discussion

Mr. H. R. HADFIELD: Has the speaker any comment to make on the use of carriers in the dyeing of blends of Acrilan and wool? The questioner has in mind, in particular, some work recently published in *Teintex* [5].

Dr. LISTER: The work mentioned refers to the application of neutral-dyeing metal-complex dyes, which are soluble in the carrier, in this case an emulsion of an organic solvent. Our own work confirms that with this type of dye the use of such a carrier increases the rate of uptake of dye, and to some extent improves penetration. The paper [5], however, dealt chiefly with the question of obtaining dark colours, and it is probable that the use of the neutral-dyeing metal-complex dyes would be ruled out for economic reasons.

Mr. W. BEAL: We have found that much less destruction of dye occurs during chroming in certain cases if an assistant such as sodium sulphite is used together with the dichromate (the sulphite being added after chroming has started). Do you feel this idea to be of practical value?

Dr. LISTER: Anything which will increase the rate of chrome lake formation is, of course, of practical value. I personally have had no practical experience of the use of sodium sulphite, but I would have expected that it would be too strong a reducing agent with the dichromate, and a similar result would be obtained to that obtained by using a chromium salt in the first place.

Several dyes can be developed on wool using chromium fluoride instead of dichromate. On the other hand, with other dyes dichromate is essential. It would be interesting to examine your results, on the effect of sulphites on the chroming of dyes on Acrilan, in terms of the behaviour of the same dyes with chromium salts on wool. A reduction in the amount of oxidising agent will, of course, bring about less destruction of dye.

Dr. L. PETERS: If chroming takes place by reaction of a nascent reduced chromium atom (before it has had time to complex with water or other ions), the presence of a reducing agent may facilitate this reaction, speeding up chroming of the underchromed parts and protecting the dye from oxidation. Dr. C. B. Stevens and I have found that simple alcohols can act as reducing agents.

Dr. LISTER: Dr. Peters' suggestion that a nascent reduced chromium atom may facilitate the chroming of dyes on Acrilan is interesting. There is some evidence for the existence of such an atom in the chroming of dyes on wool with chromium fluoride. If a dye will develop fully with chromium fluoride, our experience is that the rate of development is increased in the presence of small quantities of thioglycollic acid. Another instance, of course, is the use of thiosulphates to increase the rate of chrome lake formation of dyes on nylon.

Dr. F. MANCHESTER: Is there any advantage in running wool–Acrilan pieces in the acid alone before adding the auxiliary product and the dye?

Dr. LISTER: Running the wool–Acrilan pieces in acid alone before addition of auxiliary product and dye will even out any pH differences in the scoured

material. Our experience is, however, that it does not materially alter the solidity obtained at the end of dyeing. It is advisable for the auxiliary agent to be present in the dyebath before the addition of dye to prevent precipitation of dye acids, which are not easy to redisperse once they have been formed.

Mr. J. RANKIN*: Will the quality or type of wool used in the blend influence the solidity of colour produced by the cationic transfer method? For example, will a lower wool quality result in poorer solidity? If chlorinated wool is used, will solidity be achieved by conventional methods rather than by the cationic method?

Dr. LISTER*: The degree of solidity obtained on wool–Acrilan blends will, to some extent, depend upon the quality of the wool used, and the use of chlorinated wool will probably lead to a more solid colour. However, in our experience the most important factor is the pH of the dyebath, a reduction in pH leading to increased depth on the Acrilan, and *vice versa*.

* Communicated.

COMMUNICATIONS

A Study of the Physical State of Methylene Blue (C.I. Basic Blue 9) in Dyed Films and its Relation to Light Fading Rates

D. S. E. CAMPBELL and C. H. GILES

Methylene Blue in cast films of Cellofas A (ethylmethylcellulose) or cast or dyed films of gelatin is present as a mixture of molecularly dispersed and aggregated dye; this is indicated by the detection in the absorption spectra of the peaks of both forms (at ca. 6700 A. and 6200 A. respectively). When irradiated, the aggregated dye fades more slowly than the molecularly dispersed dye. Both forms are found to be present in the film during the actual dyeing operation. Disaggregating agents, viz. phenol, polyvinylpyrrolidone, and urea, reduce the slope of the *CF* ("characteristic fading") curve for the aggregated dye, indicating the production of a narrower range of sizes in the adsorbed micelles.

In previous papers a number of phenomena of light fading of dyes in solid films or fibres have been described and interpreted on the following hypotheses [1, 2]— (*a*) dyes are present in a heterogeneous state, partly as molecular dispersion and partly as aggregated particles of many sizes; (*b*) the molecularly dispersed material fades more rapidly than the aggregates, because fading takes place mainly at the interface between dye and the atmosphere; (*c*) any treatment which increases or decreases the proportion of molecularly dispersed dye will increase or decrease, respectively, the rate of fading.

These hypotheses have been formulated on a variety of types of indirect evidence. To obtain direct evidence by which to examine their validity a dye is required existing in monomeric and aggregated forms both of which can be readily identified, preferably before and after fading. So far as is known, Methylene Blue is the most suitable for such a test. The present paper describes a direct test of the suggestion that a dye in a solid substrate may exist as a mixture of molecular dispersion and aggregate, and that the latter fades more slowly than the former*.

Many dyes, including Methylene Blue, are, of course, known to exist in solution as equilibrium mixtures of monomeric and aggregated forms, but in nearly all cases these forms cannot be readily identified by optical means and the effect of light upon them cannot be separately studied. Methylene Blue is a notable exception, because the two forms have characteristic and widely separated bands in the absorption spectrum of the solution (Fig. 1). The effect of concentration upon the spectrum of aqueous solutions of this dye has been studied by Rabinowitch and Epstein [4] and by Lemin and Vickerstaff [5]; the last-named authors have confirmed that a band at 6670 A. is produced by the monomer and bands at ca. 6000 A. (the wavelength decreases with increase in concentration of solution) by dye in higher forms of aggregation, at first mainly dimerised (cf. Fig. 1i). With increase in concentration up to a certain limit the extinction at the latter band rises to a maximum and that at the former falls, showing that the proportion of the aggregated dye is increasing as would be expected. At higher concentrations the extinction of the aggregate band tends to fall, as the amount of dimer decreases with the formation of increasing amounts of dye at higher degrees of aggregation, whose peaks occur at shorter wavelengths, the shortest found being 5850 A.

Previously, there has been very little direct evidence of aggregated forms of a water-soluble dye being present in dry solid substrates, Astbury and Dawson's demonstration [6] of the presence of crystallites of the Solway Blues (ICI) in dry wool being, perhaps, the most satisfactory. The stage of formation of these crystallites, however, was not demonstrated, i.e. whether they were formed during the actual dyeing process or only on subsequent drying.

As long ago as 1924 Holmes [7] carried out an exhaustive investigation of the absorption spectra of solutions of many dyes of a variety of classes, and included in his paper an absorption spectrum of dry gelatin dyed with Methylene Blue, showing the two peaks, but without interpretation. The significance of his observation has, apparently, remained unnoticed.

Results and Discussion

EVIDENCE OF ABSORPTION SPECTRA

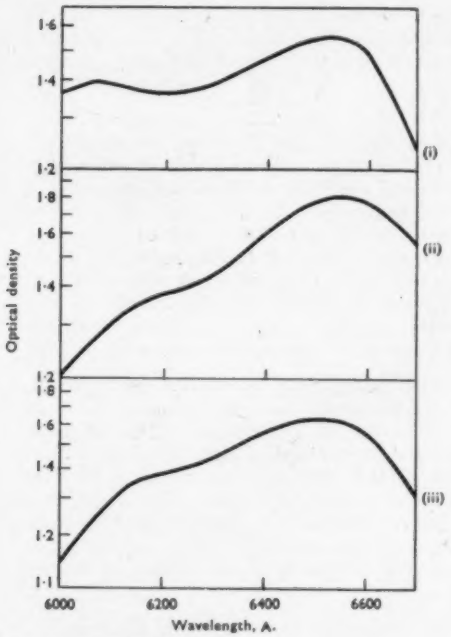
In the present work absorption spectra have been determined of Methylene Blue in various solutions and in dry films. The results show that the two absorption peaks are present in every system examined, which is interpreted as evidence that both molecularly dispersed and aggregated dye is present in all cases. (The two peaks are subsequently referred to as "aggregate" and "monomer" peaks.) The proportions of the two forms, judged by the relative heights of the two peaks, vary according to conditions. The results may be summarised as follows—

(*a*) The aggregate peak occurs at rather longer wavelengths in dry films (ca. 6200 A.) than in solution (Fig. 1).

(*b*) All dried films show the aggregate peak, and this becomes more prominent with increase in dye concentration (Fig. 2), as it does in solutions [5].

(*c*) The aggregate peak is present even in wet dyed films immediately they are removed from the dyebath, and is in fact little affected by drying at room temperature (Fig. 3). Aggregates of dye are, therefore, formed in the substrate during the actual dyeing process.

* A preliminary account of some of this work has already appeared elsewhere [3].



(i) In aqueous solution (0·001 M.)
(ii) On ethylmethylcellulose film dried at elevated temperature*
(iii) On ethylmethylcellulose film dried at room temperature

FIG. 1—Absorption Spectra of Methylene Blue

* Heated by electric lamps [cf. 9]

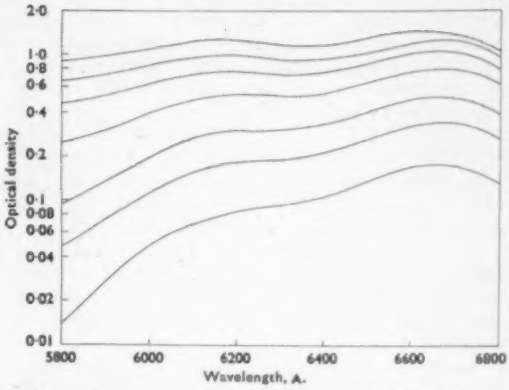
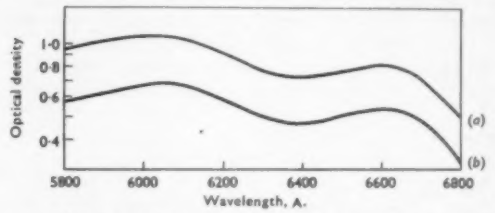


FIG. 2—Absorption Spectra of Methylene Blue at Various Concentrations in Gelatin Film (dyed at 50–60°C., dried at room temperature)



(a) 0·015 M. dye solution, dyed cold for 5 min.; spectrum before drying
(b) As (a); spectrum after drying at room temperature*

FIG. 3—Absorption Spectra of Gelatin Films dyed with Methylene Blue

* The loss of depth from (a) to (b) is attributed to migration of dye during drying.

(*d*) Phenol and urea, which are known to act as disaggregating agents for certain anionic dyes in aqueous solution [8], probably by hydrogen bonding, and the stripping agent Albigen A (BASF) (polyvinylpyrrolidone), which also must have disaggregating properties, reduce the height of the aggregate peak relative to that of the monomer in aqueous solution; also in mixtures of dye and Cellofas A, both before and after drying to a film (Table I).

The effect of these agents is not very marked, however, and is much less than that of dilution with water only (Fig. 2). In gelatin films, in fact, the effect appears to be masked altogether unless excess reagent is used. Thus, phenol, when used in the dyebath in great excess (0·25 M. solution), reduces the aggregate/monomer peak height ratio of dyed gelatin film; yet when phenol or urea or Albigen A is used in lower quantities, there is no significant difference in the peak height ratio compared with a film dyed without addition (see Table I, allowing for differences in concentration).

CONCLUSION

It is considered reasonably certain that Methylene Blue forms both monomer and aggregate† in all

† The association of basic dye molecules in solution is often referred to as "polymerisation". This term conforms with the accepted use of *monomer*, *dimer*, etc., but it is in other cases used only where individual monomeric components are covalently linked. This is unlikely to be the case here, and the term *aggregation* is therefore preferred.

TABLE I

Absorption Spectra Data for Methylene Blue

Solution or Film	Addition	Peak Optical Density Aggregate (*a*)	Monomer (*b*)	Ratio (*a*/*b*)
Cellofas A soln.	None	1·76	1·85	0·95
	Urea	1·58	1·93	0·82
Cellofas A film	None	1·90	1·975	0·96
	Urea	1·89	1·980	0·95
Cellofas A soln.	None	2·65	2·40	1·11
	Albigen A	2·52	2·42	1·04
Gelatin film	None	0·99	1·24	0·80
	Albigen A	1·19	1·38	0·87
	Phenol (0·001 M.)	1·31	1·51	0·86
	Phenol (0·25 M.)	0·39	0·78	0·50
	Urea (1·0 M.)	1·22	1·44	0·84

substrates during the dyeing process. The monomer must be present in the form of a monolayer on the internal surface of the non-crystalline regions of the substrate, and the aggregate either as discrete micelles or as a multilayer.

EVIDENCE OF MEASUREMENTS OF FADING RATE

The rate of fall in optical density at the aggregate and monomer peaks during irradiation was measured for Cellofas and gelatin films, with and without the disaggregating agents, and with various dye concentrations. The results are summarised in Fig. 4–7. As expected, in all cases the aggregated dye fades more slowly than the monomer.

"*CF*" or "characteristic fading" curves were plotted. These show the relationship between the initial dye concentration in the film and the time t_F taken for a given percentage loss (here 10%) of the original dye to occur [1]. Normally dyes present in films largely as molecular dispersion give *CF* curves of low slope (Baxter, private communication), and aggregation tends to increase the slope [1]. In the present experiments both forms of the dye give steep slopes (Fig. 7), but, with one exception, the presence of a disaggregating agent causes a considerable reduction in slope for both forms.

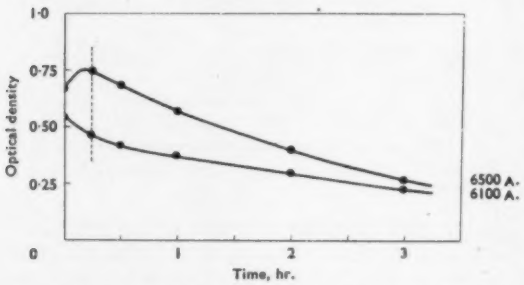


FIG. 4— Fading Rate Curves for Methylene Blue B on Cellofas A (Mercury-vapour Lamp)*

* The initial rise in the 6500 A. curve is attributed to formation of more monomeric dye by breakdown of aggregate in the heat of the lamp [cf. 2].

It is believed that the steep slopes shown here for the monomer are the result of some degree of overlap of the individual absorption curves of the two forms of dye. This overlap causes the optical density at both peaks to be composed of two components, one (*a*) due to monomer alone and the other (*b*) to aggregate, but component (*a*) predominates at 6700 A. and (*b*) at 6200 A. Such an overlap appears in fact to be clearly indicated by the shape of the absorption curves (cf. Fig. 2).

Thus fading rates at 6700 A. represent largely monomeric dye, but also some dye in several other states of aggregation. This is consistent with the steep slope of the *CF* curve. The steep slope of the 6200 A. curve would in any case be expected, because aggregated dye must be present in different states of aggregation, the range of sizes of the micelles varying with the concentration [cf. 5]. This type of system is expected to give steep *CF* curves [1].

The reduction of slope (6200 A.) caused by all three reagents means, from the theory of the *CF* curves [1], that the particle-size distribution becomes more uniform over the range of concentrations used. This could occur if the reagents preferentially attack the larger aggregates and break them down into smaller ones, but not as far as the monomeric state. The ratio of total weight of aggregate to that of monomer would then remain much the same. This situation would be consistent with the absence of any appreciable change in the relative height of the two absorption peaks; also with the fact that a large excess of phenol does increase the proportion of monomer (Table I).

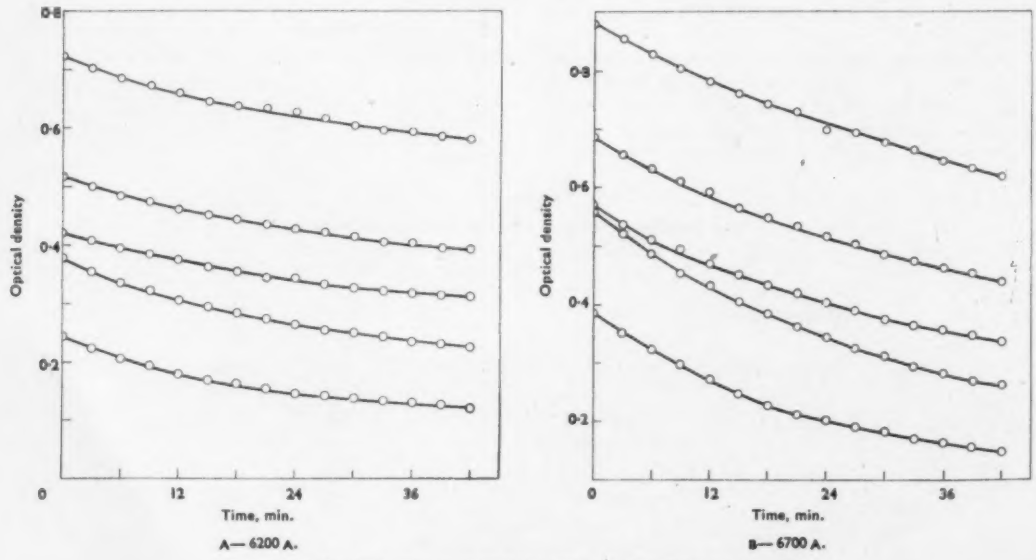


FIG. 5— Fading Rate Curves of Methylene Blue B (Xenon Lamp Exposure)

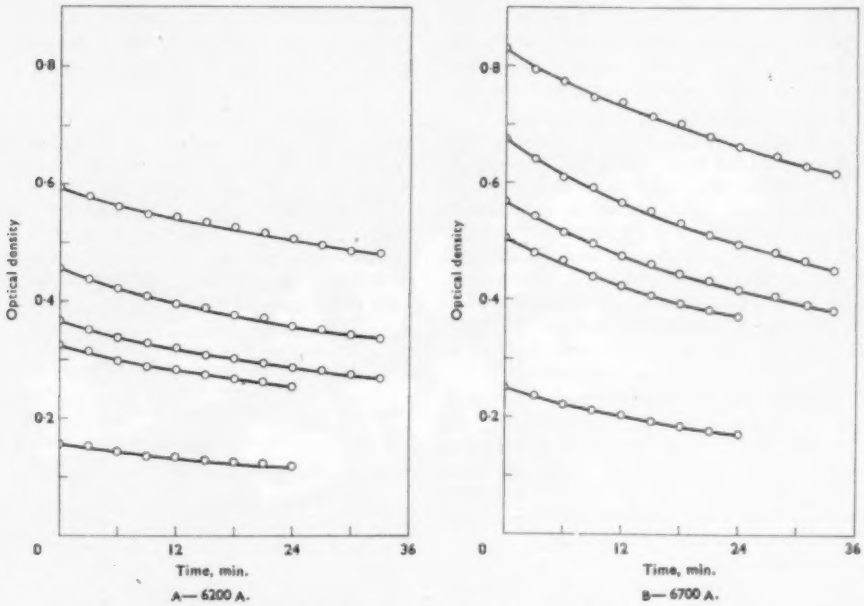


FIG. 6—Fading Rate Curves of Methylene Blue with Phenol added (Xenon Lamp Exposure)

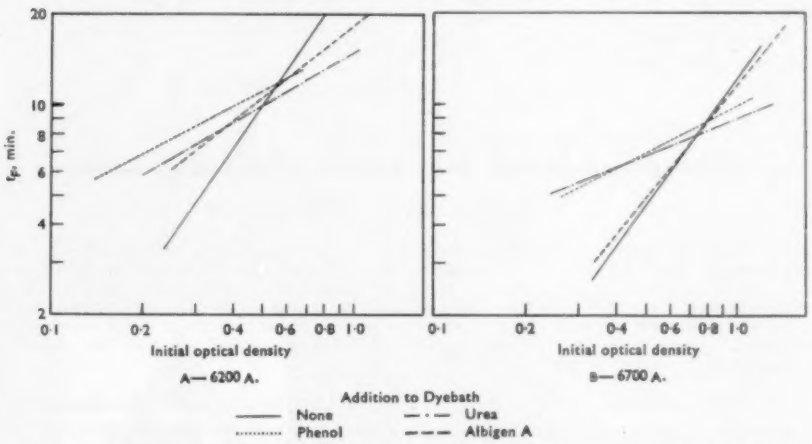


FIG. 7—*CF* Curves for Methylene Blue Fading in Gelatin Films with and without Disaggregating Agents (for clarity the experimental points are omitted)

The change in slope which occurs with the 6700 A. *CF* curves in two cases must be the result of the overlap effect discussed above.

EFFECT OF EXCESS PHENOL ON FADING

It was found that when a very large excess of phenol (0·25 M. solution) was used in the dyebath, the absorption spectra of dyed gelatin films showed the expected reduction in the proportion of aggregate, but the fading was abnormally slow. The rate was in fact only about one-tenth of that of the films dyed with smaller quantities of phenol. This phenomenon was not further investigated, but it is clear that excess of phenol acts as a fading inhibitor, by either a chemical or a physical mechanism.

Experimental

The Methylene Blue used was a sample of the highly pure BPC (ICI) brand, recrystallised from ethanol.

4% Ethylmethylcellulose (Cellofas A (ICI)) solution (centrifuged to remove fibrous matter) (7 c.c.) and 6% pure photographic gelatin solution (6 c.c) were used for making the films by spreading on 4 in × 2·5 in. "subbed"* glass photographic plates.

The technique of preparing, drying, irradiating, and measuring the fading rate of the films has already been described [1, 9].

Cellofas A films with dye incorporated during formation were prepared by adding varying

* Plates treated superficially after manufacture to key a gelatin layer to the surface.

quantities (between 1 and 6 c.c.) of 0·001 M. dye solution before spreading. Albigen A (BASF) was added in 1-c.c. portions of the commercial liquor. Urea was used in equimolar proportion with the dye.

The hardened gelatin film was prepared by treating a cast and dried film in 10% formaldehyde (40%) solution cold for 2 hr., and then thoroughly rinsing. The dried film was then immersed in 10 c.c. of Methylene Blue solution in concentrations between 0·01 and 0·1 g./litre at 50–60°C. for 30 min., and was afterwards well rinsed and dried. The dyed films appeared under the microscope to be evenly penetrated. Additions were—Albigen A (2·5 c.c. commercial liquor per 100 c.c.), phenol (2 moles per mole of dye; also in 0·25 M. concentration), urea (1·0 M. concentration).

In the earlier stages of the work mercury-vapour light was used for irradiation (cf. Fig. 4). Later, a xenon (BTH) lamp was used in the same apparatus [cf. 9]. This gives a close approximation to sunlight [10], but the low-power lamp used here does not appear to cause any overheating of the films, so that disaggregation effects due to heat in fading are minimised.

Mercury-vapour light consists mainly of monochromatic light of a few wavelengths. One of the principal lines in the emission spectrum (see Fig. 23 [9]) lies close to the absorption maximum of the dye polymer at ca. 6200 A., but there is no line close to the monomer peak at 6700 A. This illumination will therefore tend to cause the monomer to fade more slowly than the polymer, and so will tend to mask the difference in fading rates between the two forms.

* * *

The authors thank Professor P. D. Ritchie for his encouragement and interest; Mr. R. B. Collins and Ilford Ltd. and Dr. M. A. T. Rogers and Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of materials; the Wool Textile Research Council for a grant for purchase of materials and a scholarship to one of them (D.S.E.C.); and Mrs. P. Catchpole for assistance with experimental work.

COLOUR CHEMISTRY RESEARCH LABORATORY
DEPARTMENT OF CHEMICAL TECHNOLOGY
ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY
GLASGOW C.1

(*Received 10th September 1957*)

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A Dye-uptake Meter for Studies of Dyeing Kinetics

E. BAKKER and D. PATTERSON

An apparatus for measuring the rate at which dye is transferred from dyebath to fibre is described. It differs from previous forms of apparatus in that no special device for circulating the solution through a separate observation cell is required. Instead, the observation cell is formed within the dyebath by two inverted "periscopes" facing each other at a fixed distance. A simple double-beam optical system provides a means of eliminating the effects of any drift in the output of the light source or in the sensitivity of the light-measuring system. The types of experiment which can be carried out with the apparatus are mentioned and some examples given.

Introduction

The basic process that is investigated in all studies of dyeing kinetics is the transfer of dye from the bath into the fibre. The rate at which this occurs can be measured in a system containing a fixed quantity of dye by measuring, as a function of time, either the decrease in concentration in the dyebath or the increase in concentration in the fibre.

The determination of dye concentration in the fibre usually entails a multiplicity of experiments in which different samples are dyed in separate baths for each dyeing period, and this may introduce errors owing to differences among samples and baths. In cases where the quantities of dye transferred to the fibre are small, a number of samples can be dyed together in a single bath, and individual samples removed at suitable intervals without sensibly altering the dyebath concentration, but the method is time-consuming. A further factor that must be guarded against in this type of experiment is that the rate of dyeing should not be altered by the change in the effective liquor ratio as samples are progressively removed for analysis.

There are thus many advantages in measuring the change in concentration of dye in the dyebath, since the whole course of the dyeing can be followed with one sample and all the disadvantages mentioned above are avoided. In cases where new dyes are being tested or special purification methods employed, there are obvious gains in reducing the quantities required. It must, however, be recognised that, since the quantity of dye in the fibre is of primary interest, the method is an indirect one, and care must be taken in each particular case to ensure that dye passing from the bath does in fact enter the fibre and is not being lost by chemical decomposition or physical deposition in some other part of the system.

The advantages of measuring dyebath concentrations have naturally not passed unnoticed, and apparatus for making this measurement has been described before by Speakman and Smith [1],

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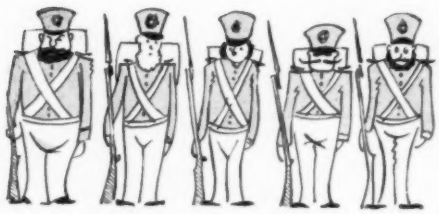
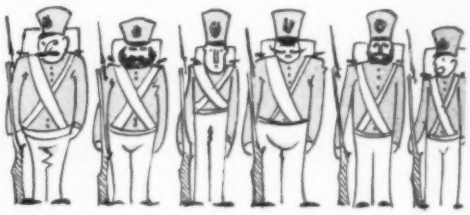

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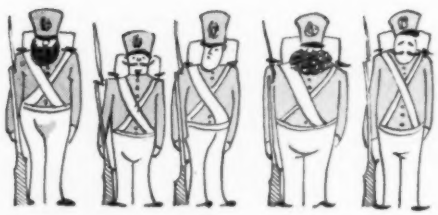
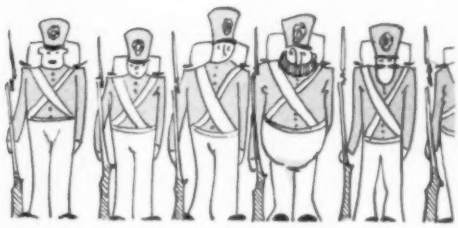

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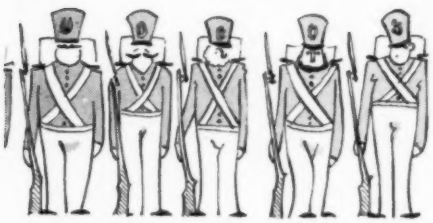
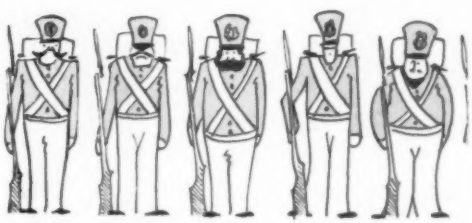

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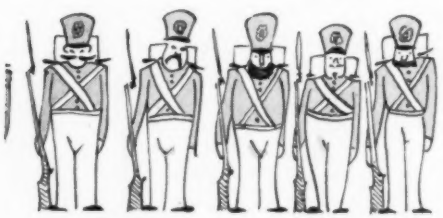
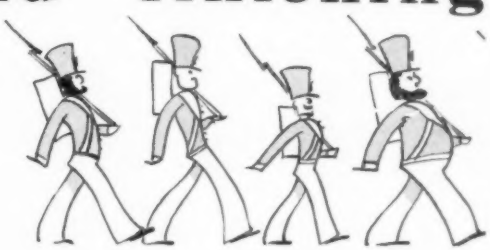

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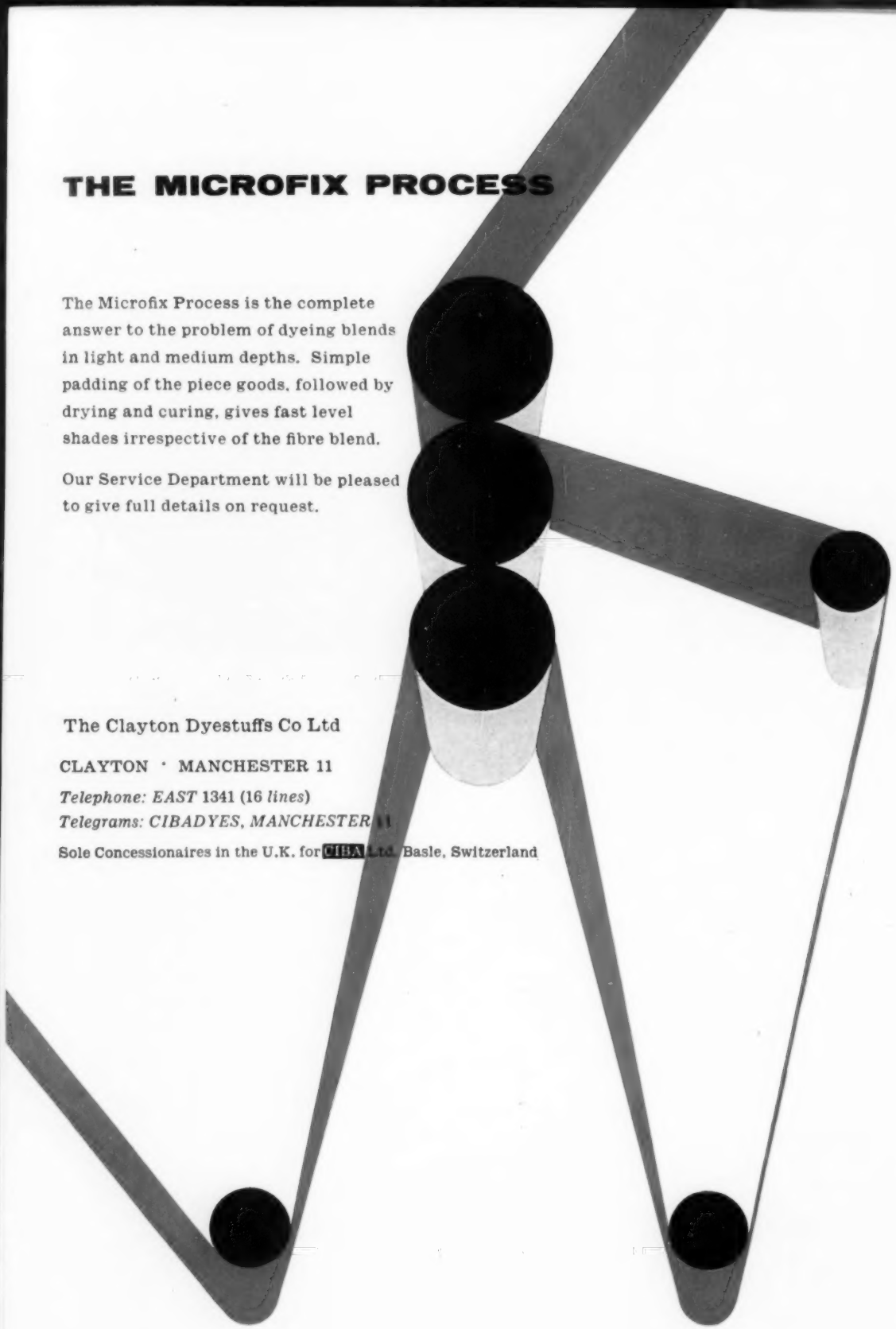

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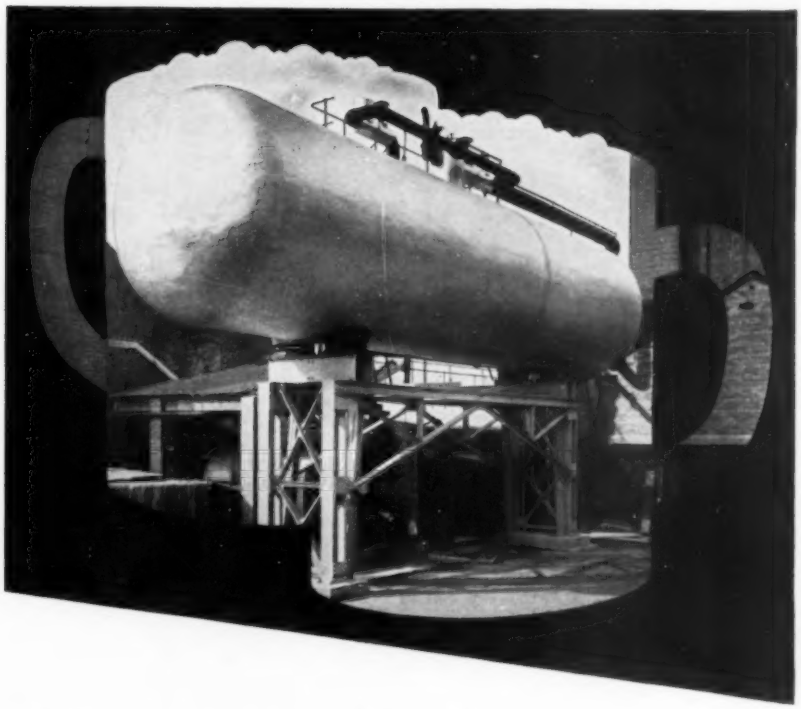

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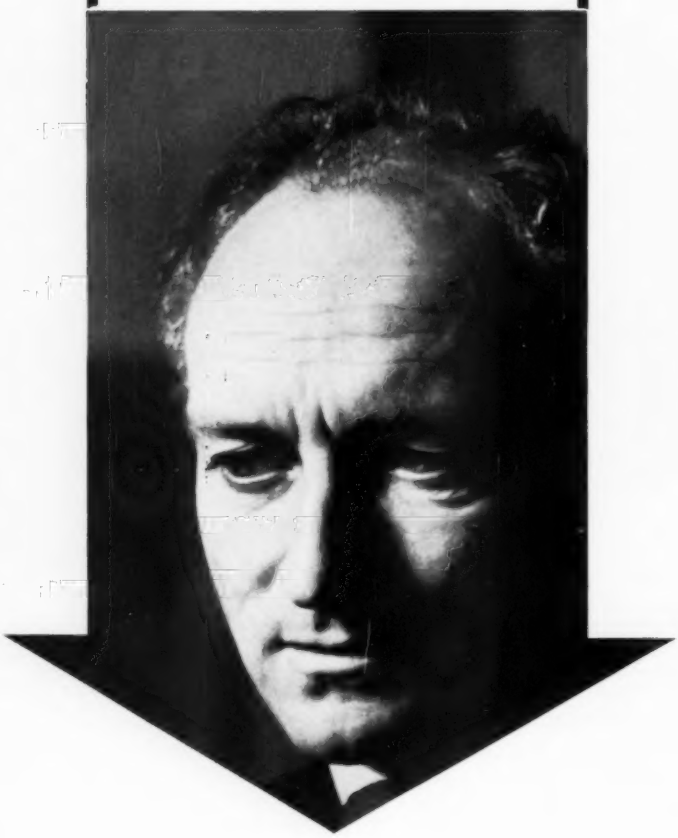

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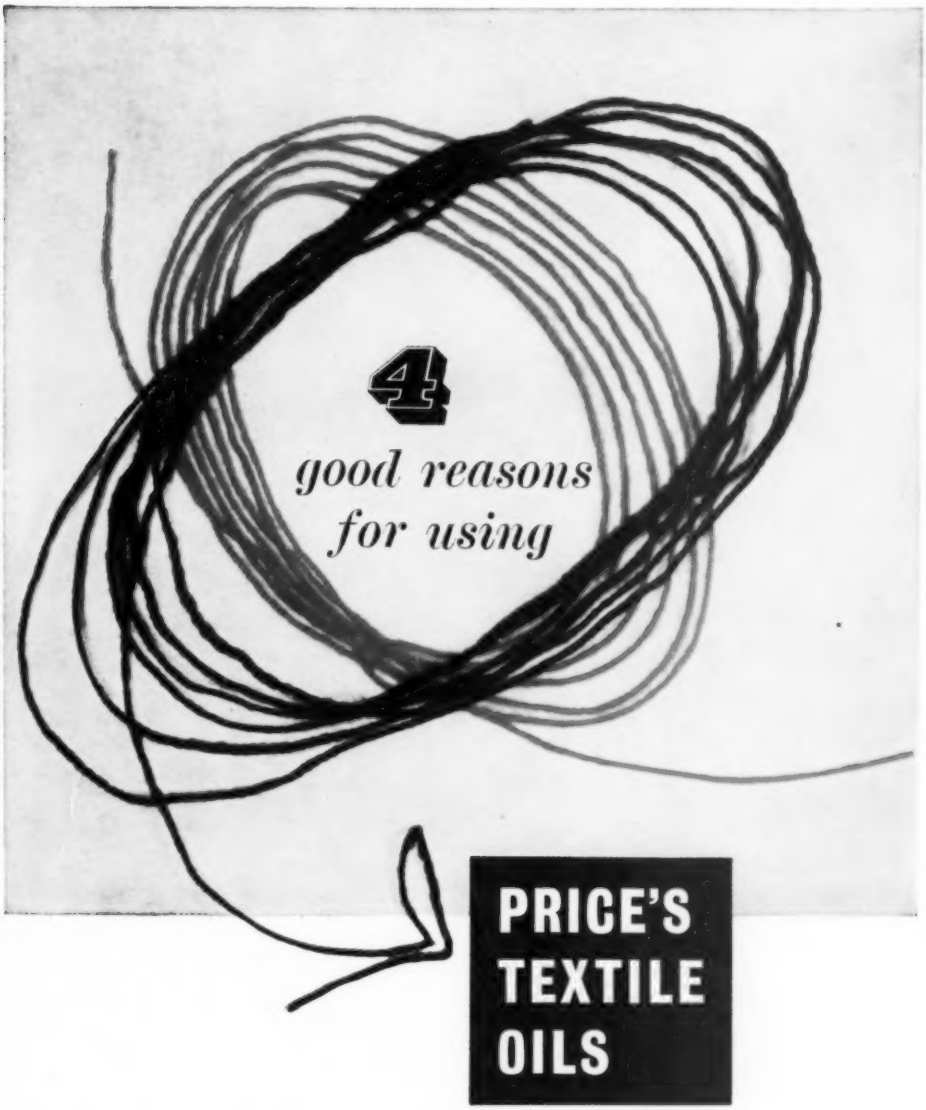

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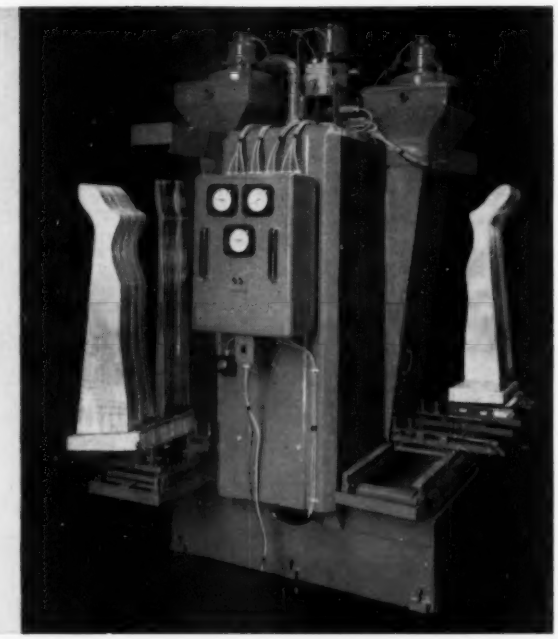

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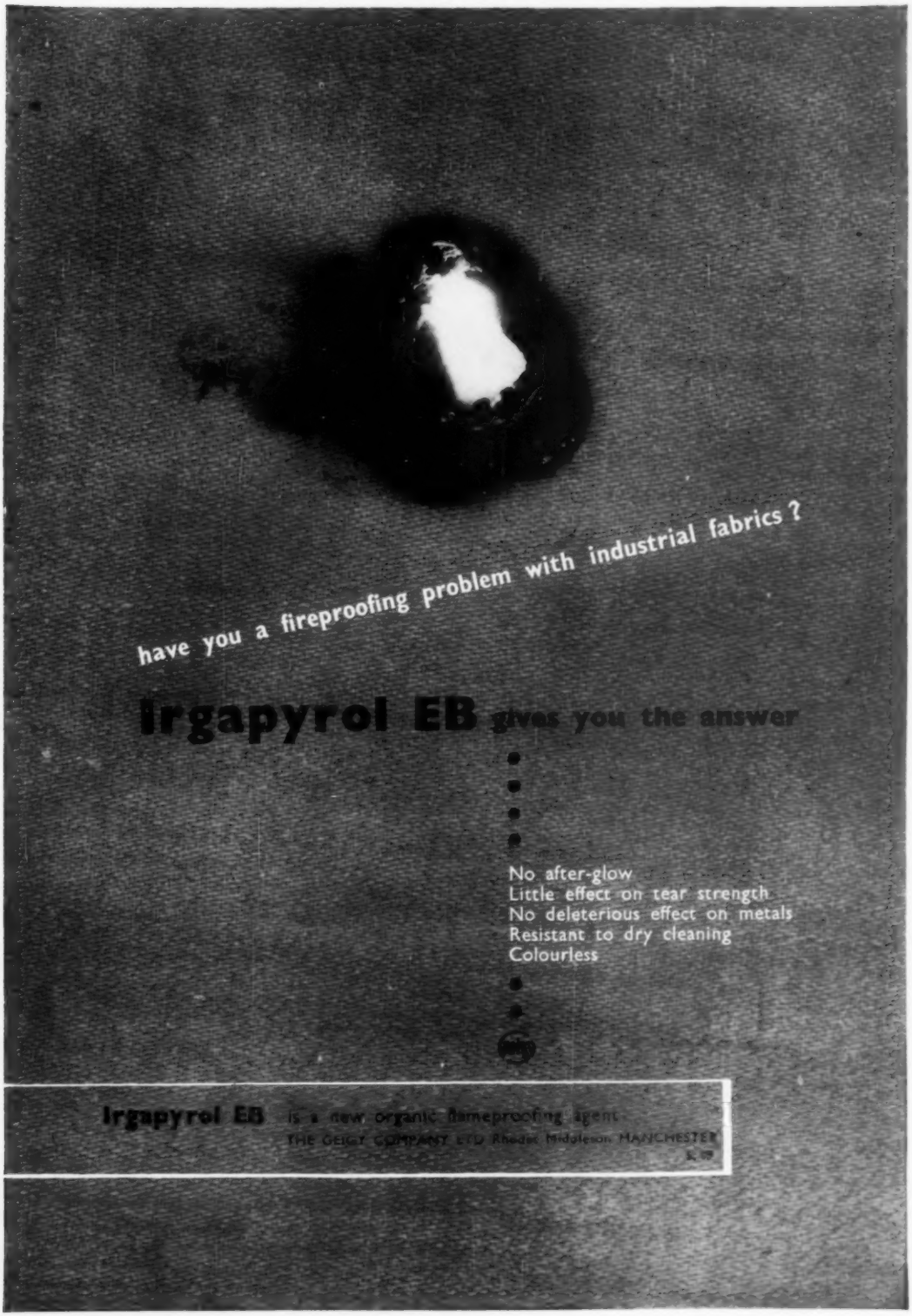
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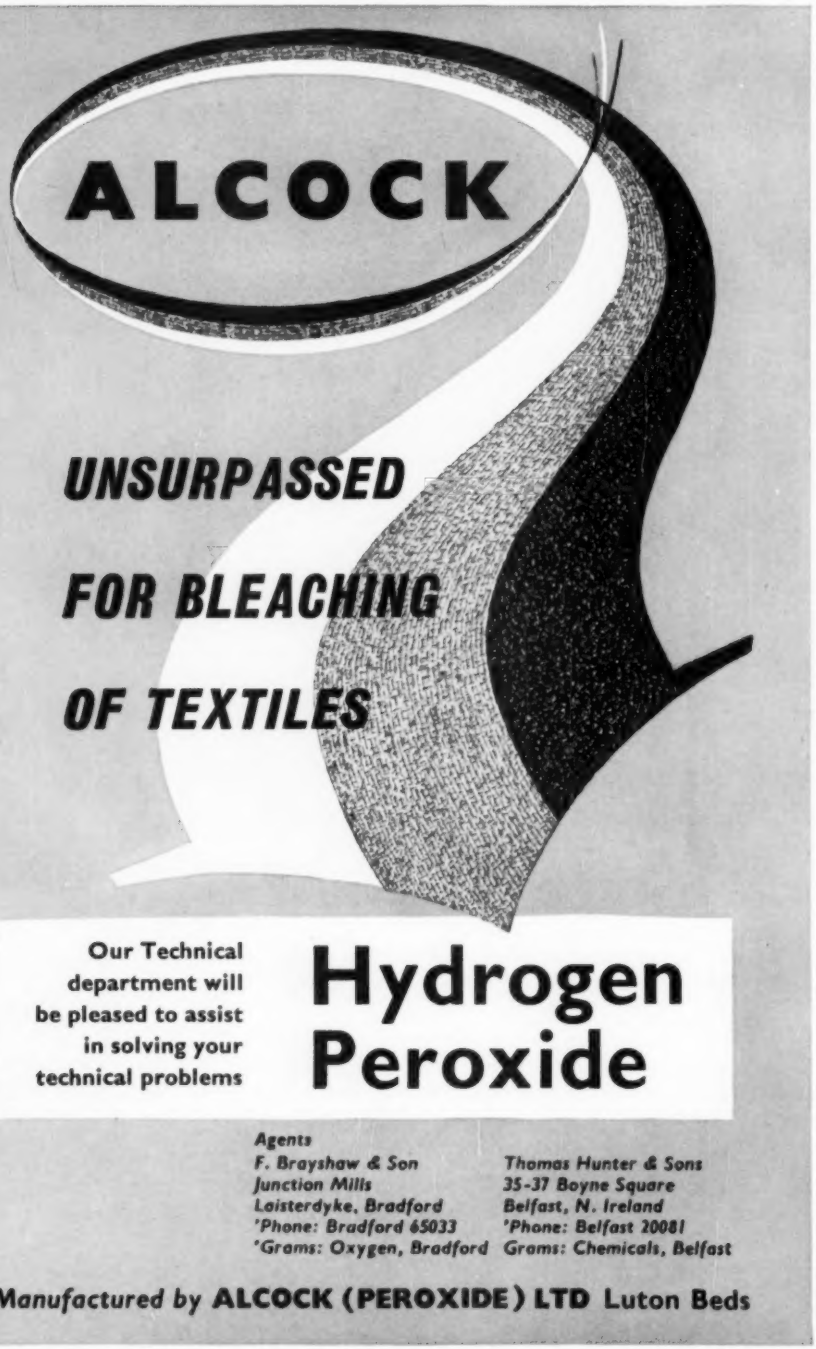

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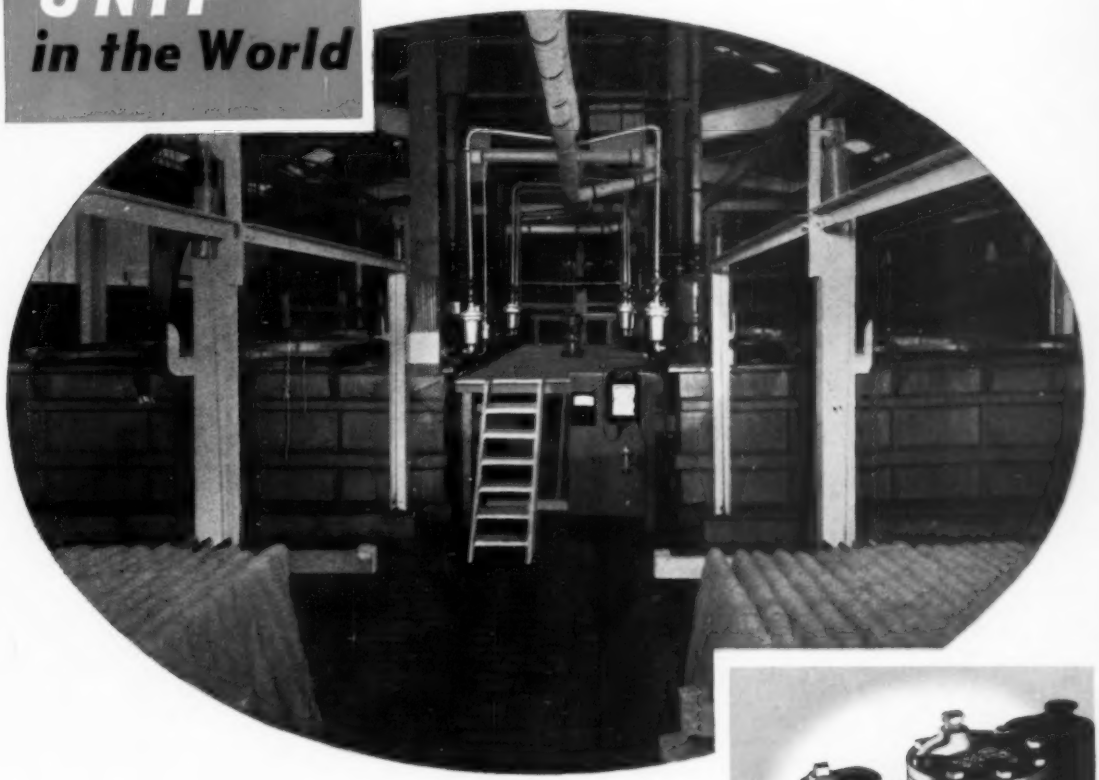

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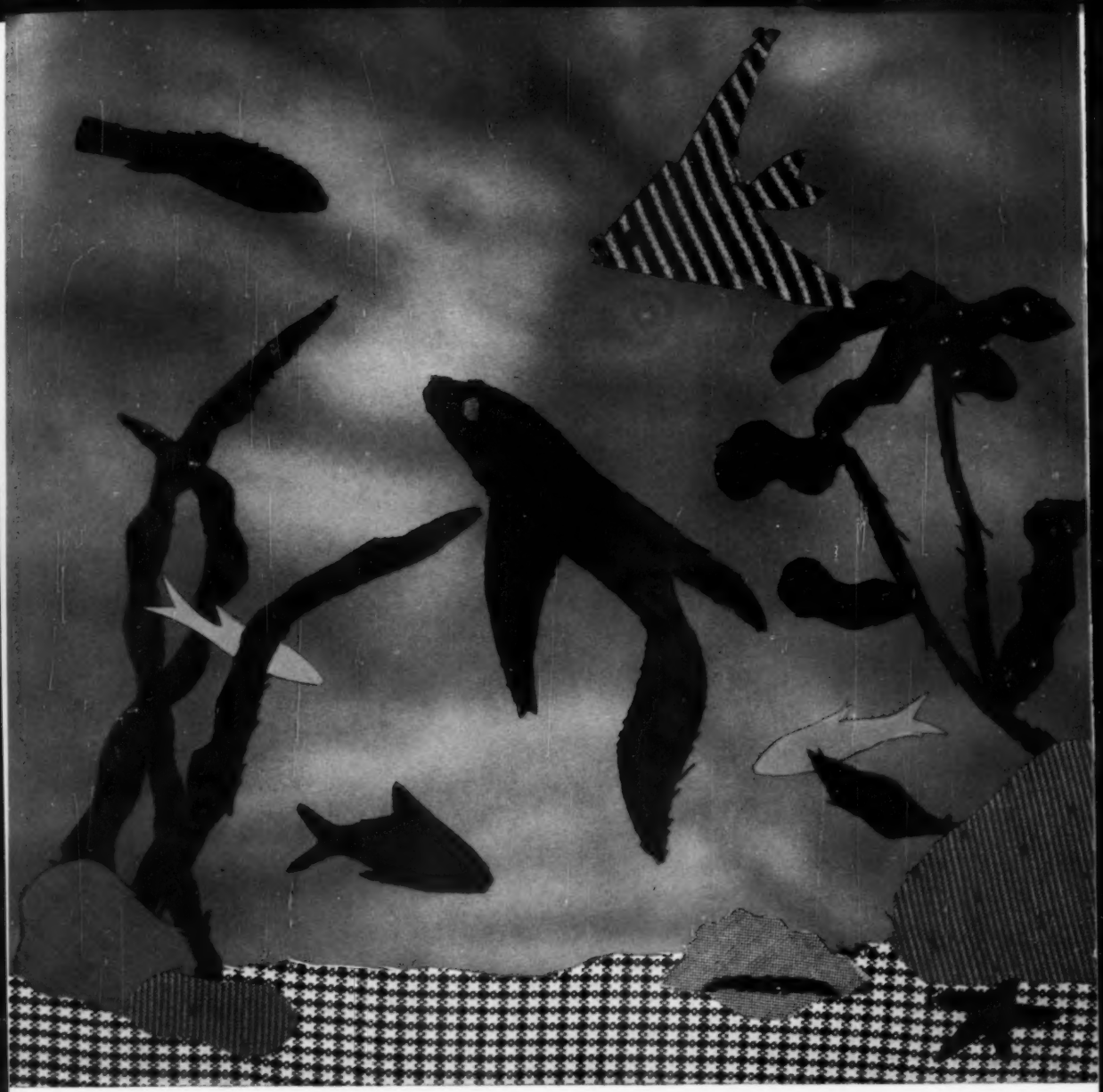

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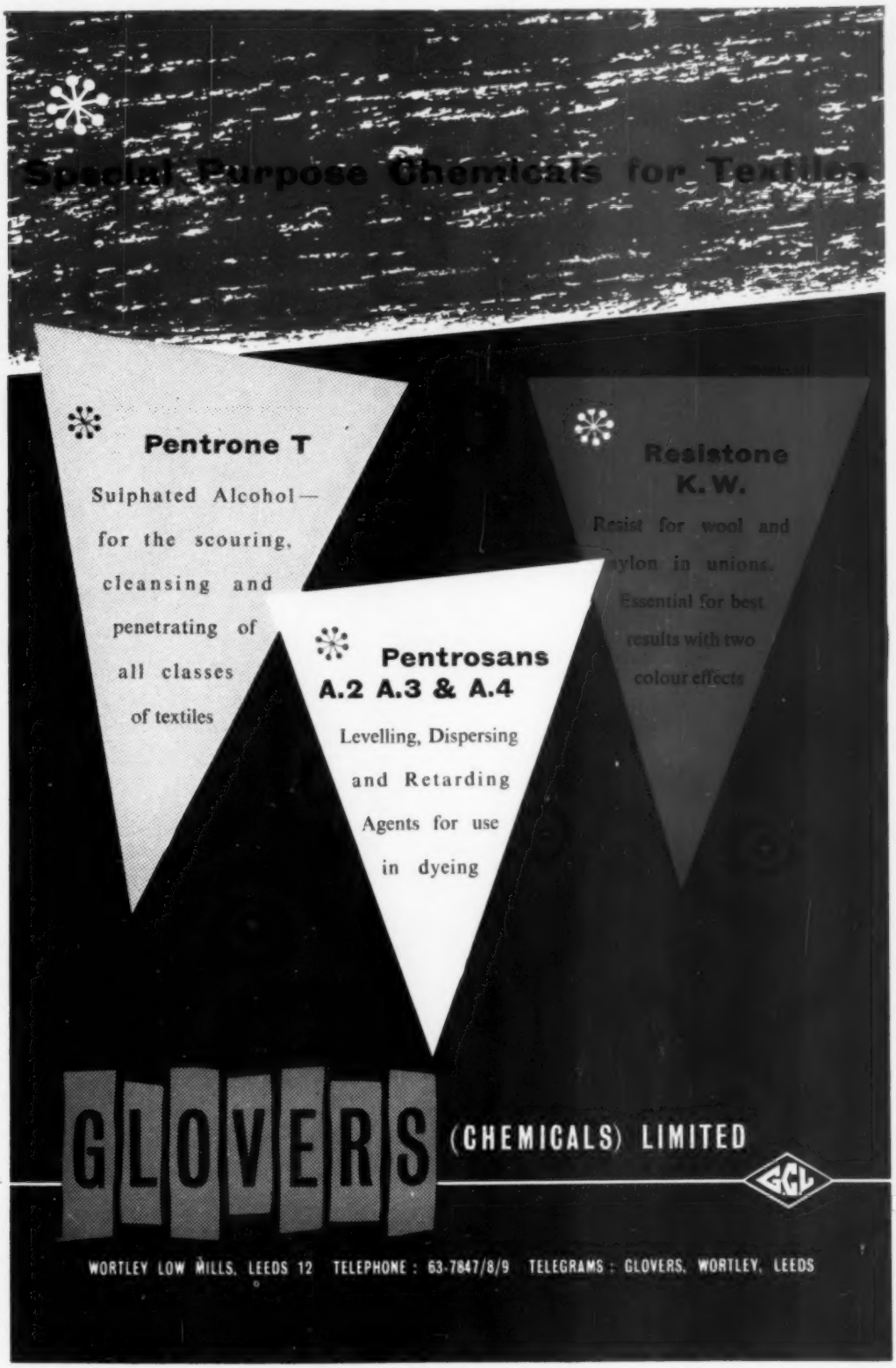
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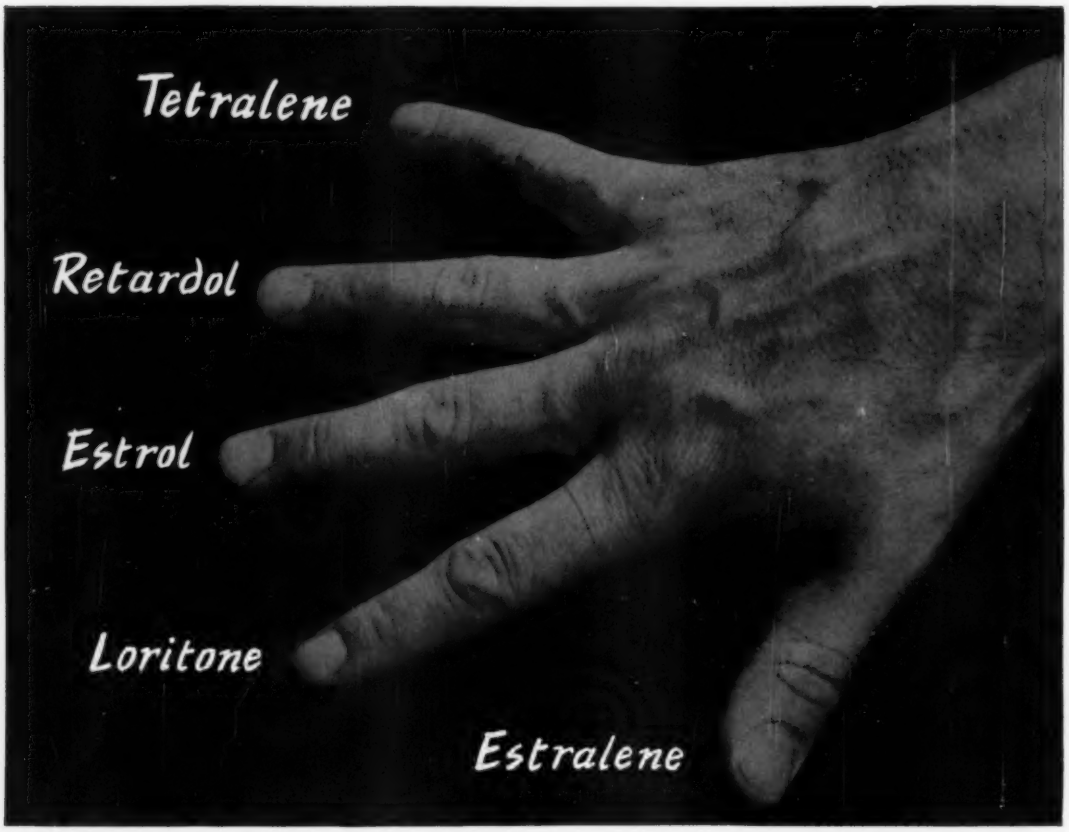

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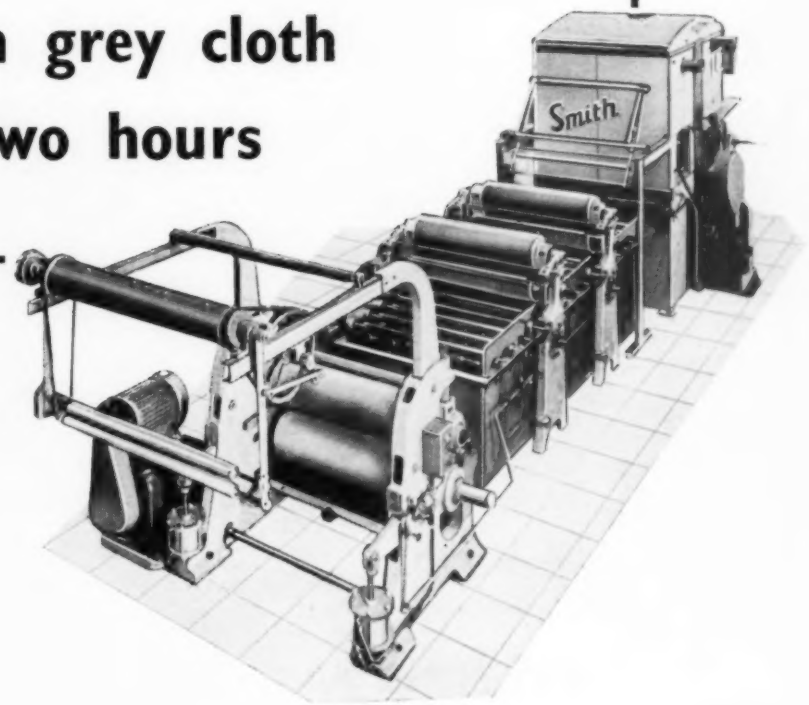

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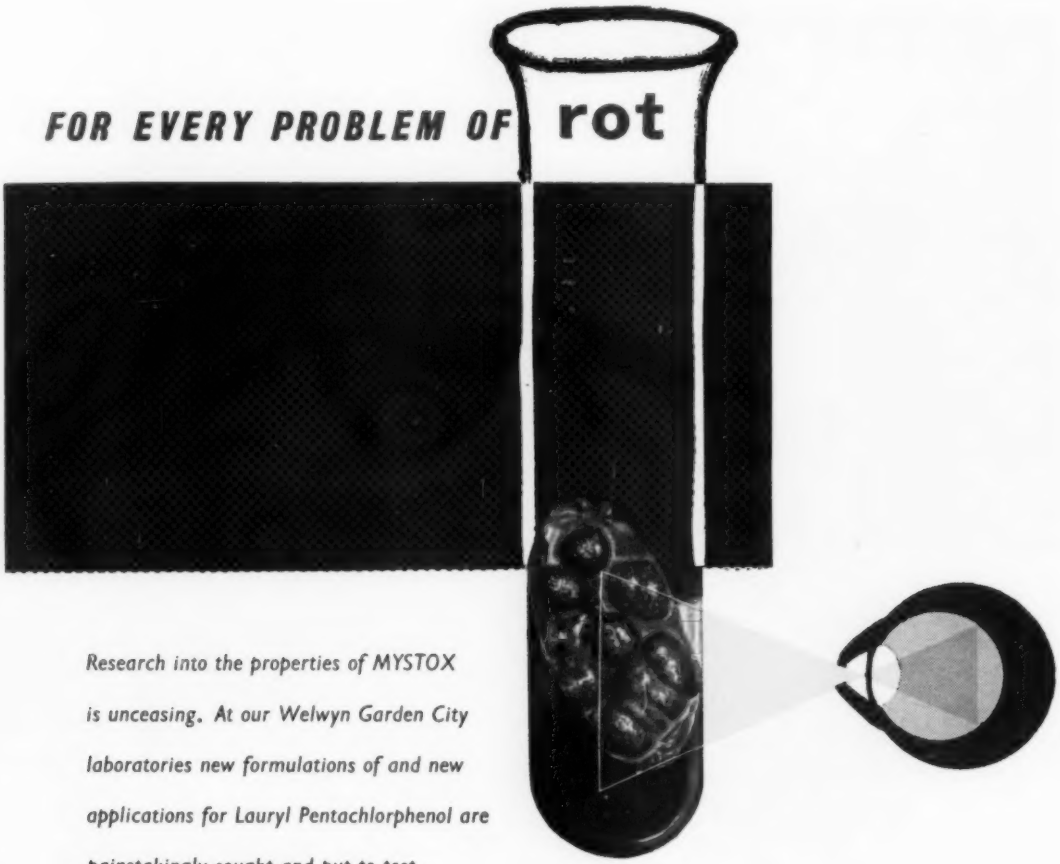

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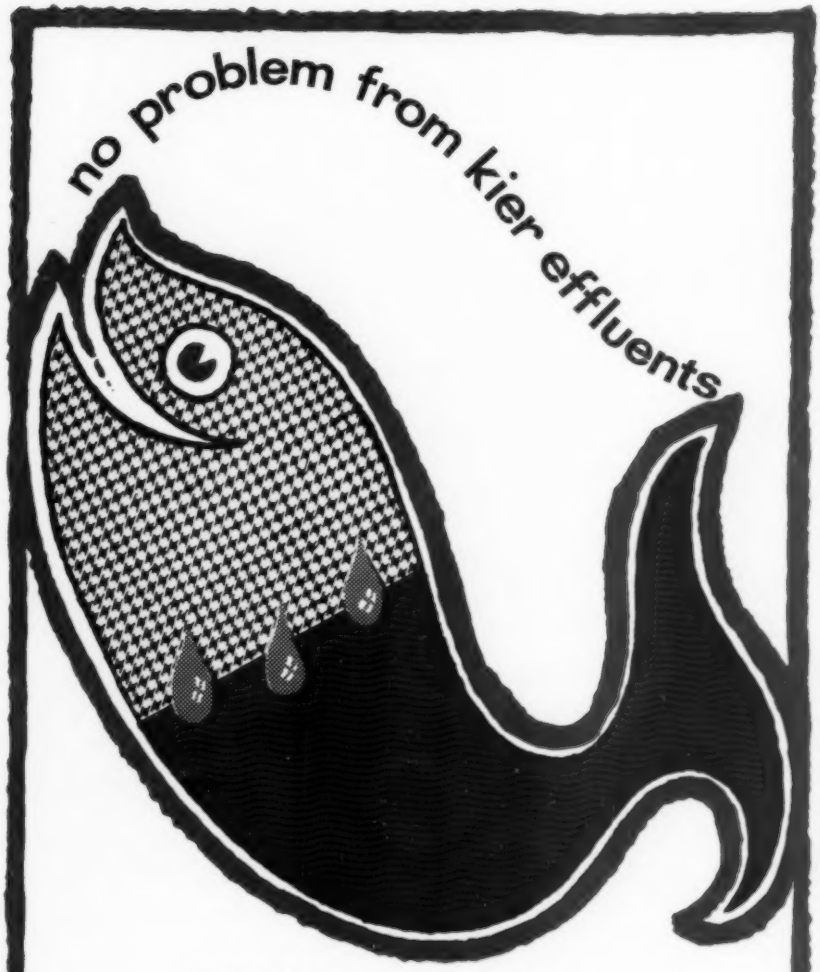

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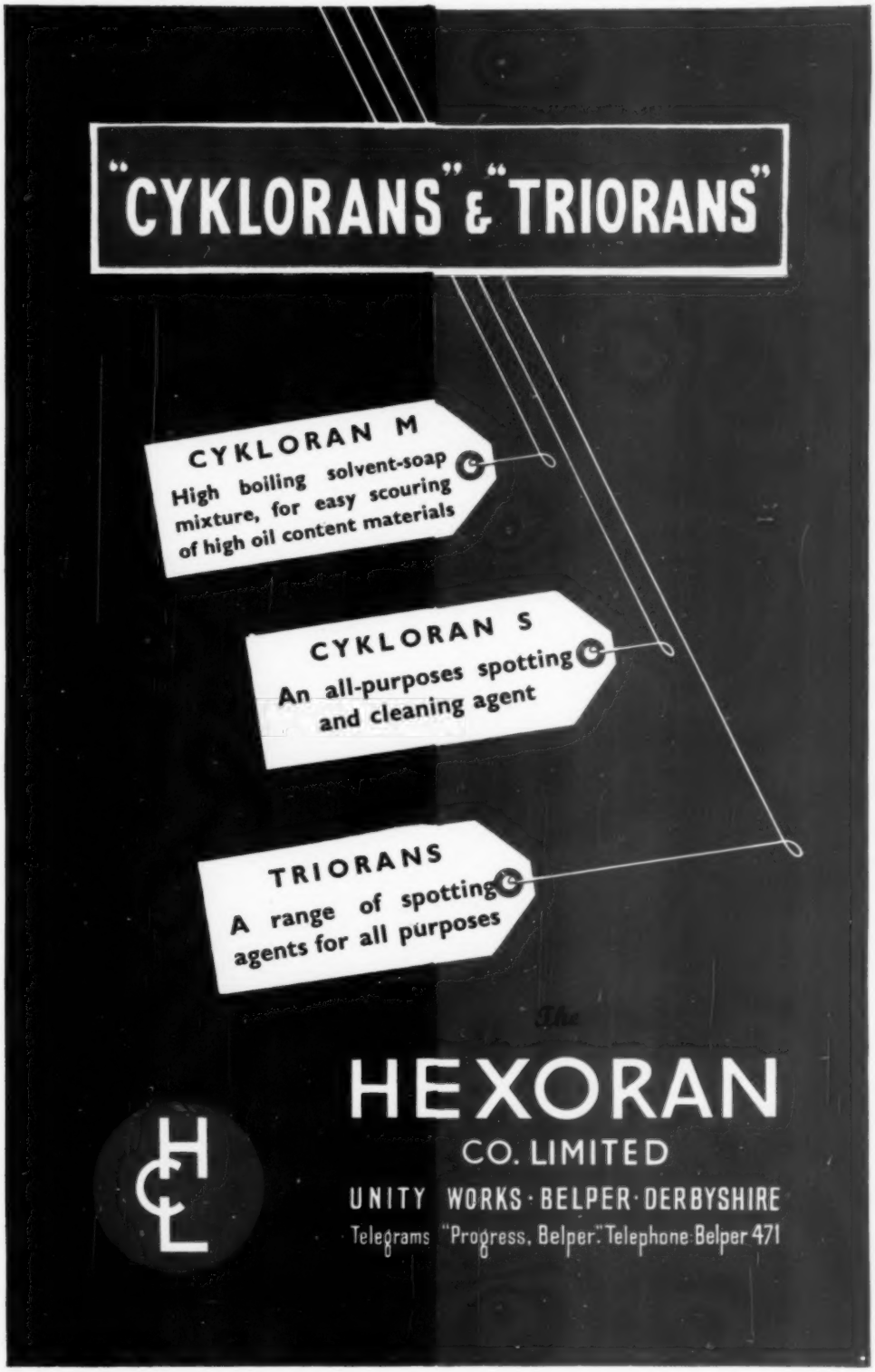
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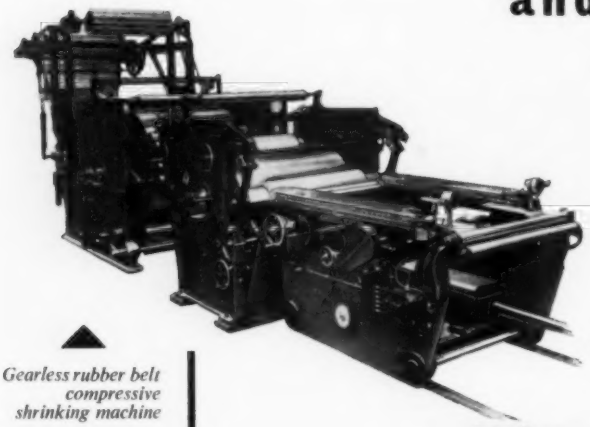

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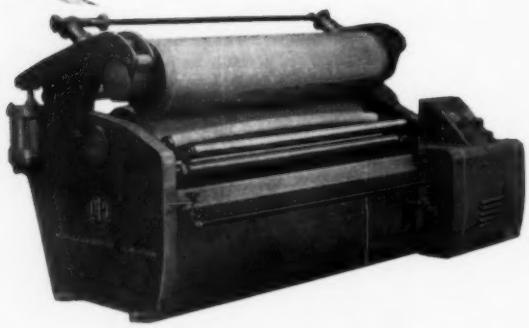

Two-bowl pneumatic off-set padding mangle

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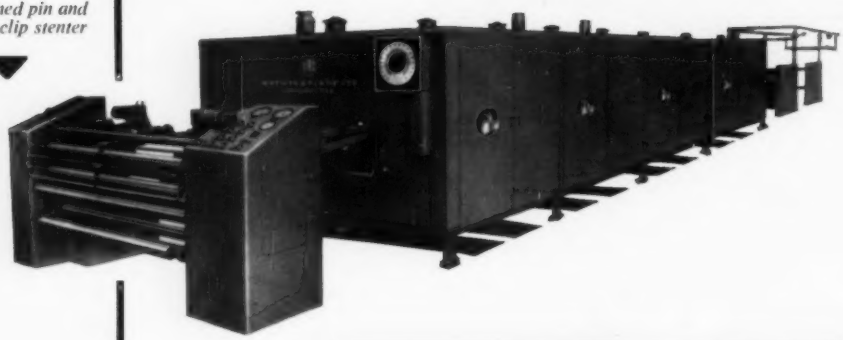

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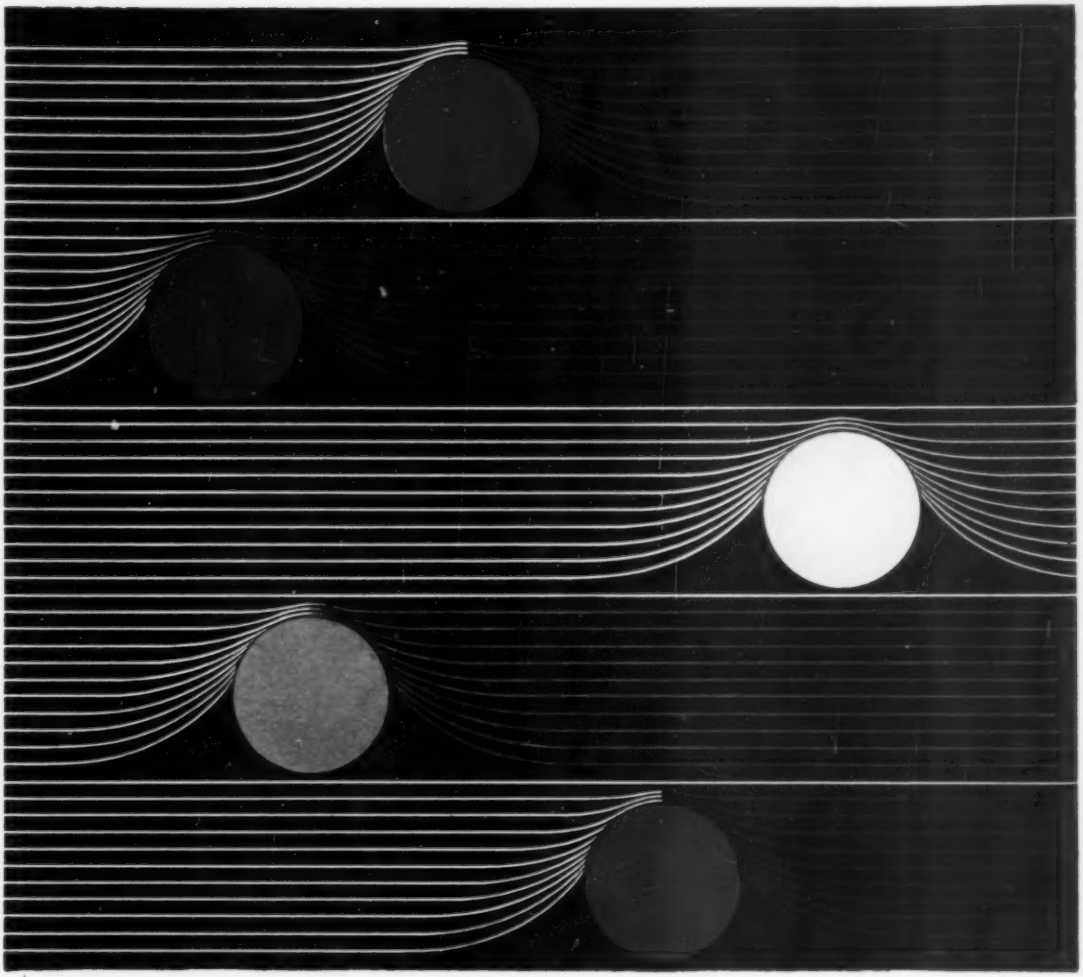

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Davenport [2], Kienle, Royer, and McCleary [3], and Chamberlain and Lister [4]. The present apparatus is, however, simple, and conditions of dyeing are more like those in an ordinary laboratory dyeing machine, since in each of the earlier designs some of the dye liquor is circulated through a separate optical test cell.

Description of the Apparatus

GENERAL PRINCIPLE

The new feature of the apparatus is that an absorption cell is formed within the dyebath by means of a pair of inverted periscopes which face one another as shown in Fig. 1. The method of operation can be understood from Fig. 2. There are two paths by which light can pass from the source to the photomultiplier. The purpose of the non-absorbing path *A* is to provide a reference signal, so that slow drifts in the light output of the lamp or the detector system are compensated. Light traverses either the absorbing path *B* through the dyebath or the non-absorbing path *A*, according to the position of the rotating sector *R*, which is of the form shown in Fig. 3. When the sector blanks off the absorbing path for a short period during its rotation, light following path *A* passes through the hole to the photomultiplier. After suitable initial balancing of the intensities of light traversing the two paths, the optical density of the dye in the bath can be calculated from—

$$\log \frac{I_0}{I}$$

where I_0 is the intensity of light following path *A*, and I that emerging from path *B*.

Provided that Beer's law holds, the measured optical density will be directly proportional to the dyebath concentration. If Beer's law does not hold for a particular dye solution, a calibration curve can be prepared by using the apparatus to measure the optical density of solutions of known concentration and plotting a graph of the results. The necessary corrections can then be applied to subsequent readings. In practice, by proper selection of colour filters as described later, this has not been found necessary.

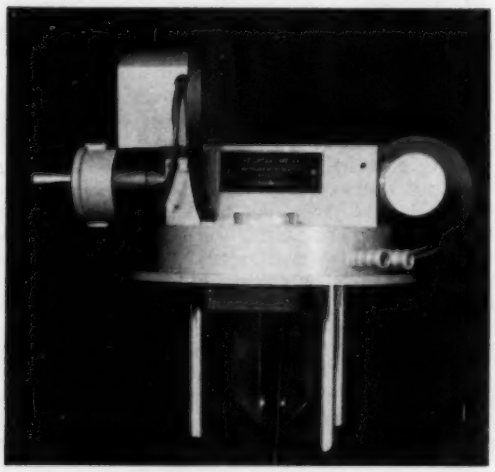


FIG. 1

DETAILED DESCRIPTION

(*1*) *Optical Train*

The light source is a 6-volt 24-watt car headlamp bulb run at 4 volts from an accumulator. A voltmeter is connected across the terminals so that it is immediately obvious if the battery is discharged. Under-running the lamp helps to diminish changes in light output with voltage, and by charging the battery each night after a day's run, no trouble has been encountered. The lamp *X* is placed at the focus of a planoconvex lens *Y* of about 5 cm. focal length, so that parallel light emerges on to the stop *C* (Fig. 2). This has two apertures which define two light beams following paths *A* and *B*. The rotating sector *R* allows the light to follow one or other of these paths in the manner previously described. The sector is driven by a small synchronous motor (Everett, Edgecumbe type MBH) at a speed of 1 r.p.m. or 1 r.p.h. according to the duration of the dyeing experiments being carried out.

The light beam travelling along path *A* first meets an iris diaphragm *E* (Fig. 2) used for altering I_0, the reference light intensity, when carrying out the balancing operation, which is described later. Next there is a second stop *L* similar to *C*, to

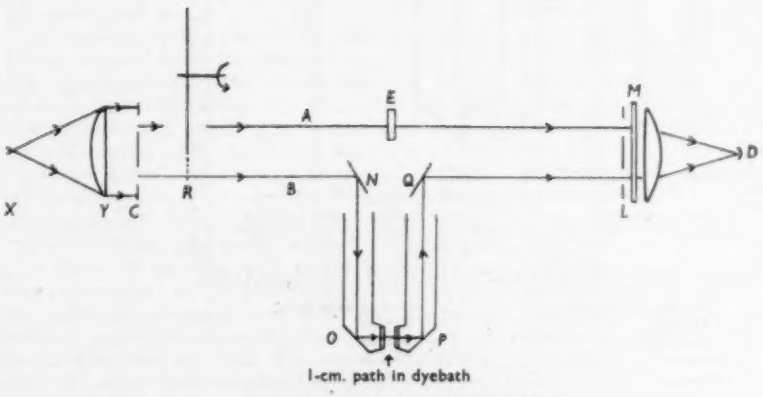


FIG. 2—Diagram of Optical Path

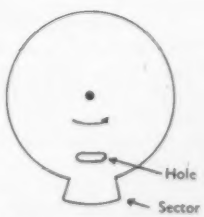


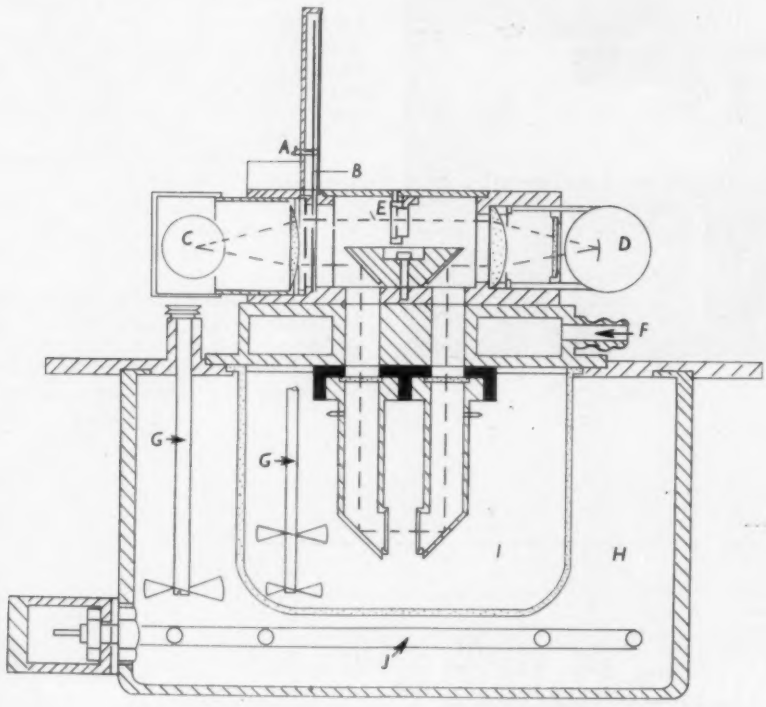
FIG. 3—Rotating Sector

cut down scattered light, then a colour filter *M*, and finally a second lens similar to the first, which focuses an image of the filament on the sensitive surface of the photomultiplier *D*.

Path *B* is similar to *A* as far as the rotating sector, but after this the light suffers reflection at a mirror *N*, inclined at 45° to the vertical, which directs it down a tube dipping into the dyebath, and at the bottom of the tube is a second mirror *O* parallel to the first. After passing through a plane window the light enters the dyebath and is absorbed to an extent proportional to the concentration of dye in the bath. The unabsorbed light passes through the window of a second similar "periscope", is reflected up it by the mirror *P* at the bottom, and then is again reflected by another mirror *Q* at the top. It is finally focused on to the photomultiplier *D* in a manner exactly similar to the light in the non-absorbing path.

The colour filter *M* is chosen to have its maximum light transmission at the peak absorption wavelength of the dye in the bath. The latter value is found by determining the absorption spectrum of the solution with a spectrophotometer such as a Unicam SP 500. A suitable filter can then be selected from the published absorption curves of Wratten filters[5] or by the use of a dichroic interference filter, such as those of Barr & Stroud, which have a single narrow transmission

FIG. 4



A Clock motor (1 r.p.m.)
B Chopper
C Lamp (6 v, D.C.)
D Photocell
E Iris
F Cooling water jacket
G Stirrers
H Oil-bath
I Dyebath
J Heater (1 kw.)

FIG. 5—Sectional View of Dye-uptake Meter

band at any desired wavelength in the visible spectrum. So that filters can readily be changed, a locking screw is provided on the housing of the optical path, which, when released, allows the photomultiplier and its housing to be withdrawn from the apparatus (Fig. 4).

(2) *Measurement of Light Intensity*

The light intensity is measured with the aid of an RCA 931A photomultiplier tube. The power supply for the tube is a well stabilised D.C. power unit (Isotope Developments EHT unit type 532), and the photocurrent is indicated on a Pye Scalamp galvanometer and recorded on a Fielden Servograph with a full-scale deflection of 50 μa. A variable shunt resistance has been provided in the recorder so that higher light levels can be used if need arises. The upper limit of linearity of photocurrent with light intensity is 10 ma. at 100 v. per stage accelerating potential for the type of photomultiplier used [6], so that the normal operating conditions are well below this limit. Very good stability is obtained after allowing about 15 min. for warming up, but since a reference calibrating signal is recorded once each revolution of the rotating sector (normally once a minute), no difficulties are encountered from any slow drift that may occur.

(3) *Mechanical Construction*

A general view of the apparatus is shown in Fig. 4, and a sectional view of the dye vessel in Fig. 5. The dyebath vessel I is of glass and is surrounded by an outer tank H filled with glycerol and heated by an electric immersion heater J controlled by a bimetal controller. Rapidly rotating stirrers G are fitted, and the relatively large heat capacity of the thermostat smooths out short-term fluctuations which could arise from the on–off action of the heater.

All the parts of the optical system are attached to the lid of the dye vessel itself, which is fitted with three legs so that the lid and its attachments can be removed and stood on the bench without damage to the optical parts (Fig. 1). The lid is also provided with a jacket F, through which cold water is circulated from a constant-head supply, so that the metal parts do not conduct heat to the lamphouse C, rotating sector B, mirrors, and photomultiplier D.

Construction of the periscopes was not accomplished without some troubles. They were made from square-section brass tube, and the metal mirrors at the bottom were cut from photographic glazing plates and soldered in position. The two windows sealing each upper end were then fixed in position using a minimum amount of Araldite thermosetting resin. It was found essential to fit a small open tube to each periscope to allow for the expansion of the air inside when the periscopes were placed in an oven to cure the resin. These tubes were sealed off soon after removal from the oven, when the air inside was quite dry. By these methods early difficulties due to condensation on the windows were avoided. The upper ends of the periscopes were fixed to a Sindanyo block (shown in black in Fig. 5) to minimise heat conduction to the cooled lid, on to which the whole assembly was screwed.

The bearing of a stirrer for the dyebath was also mounted in the lid, the drive for this stirrer being taken by a rubber belt from a pulley mounted on the shaft of the stirrer in the thermostat bath (Fig. 4). Provision was also made in the lid for the insertion of a thermometer into the dyebath. Another hole in the lid, which was closed by a metal stopper, allowed the introduction and removal from the dyebath of fibre samples enclosed in a stainless-steel cage.

Method of Operation

The apparatus can be used in three principal ways—

(1) To measure the rate of transfer of dye from the bath to an undyed fibre.

(2) To measure the rate of desorption of dye from a dyed fibre into water.

(3) To measure rates of dyeing at constant concentration of the dyebath. The uptake of dye by the fibre is then compensated by measured additions of further dye solution.

In all cases it is necessary to carry out an initial balancing operation, and this is done after allowing about 15 min. for the lamp and photomultiplier circuits to warm up and reach equilibrium. There is always an initial fall in the output of the photomultiplier under illumination, and it is more convenient to pass this point before measurements are begun. During this period the dye vessel is filled with the necessary amount of water in the case of experiments of the first two types, but with dye solution in the third type, and is brought to the required temperature. All water used must have been previously boiled to expel dissolved air.

The balancing operation is then effected by means of the iris diaphragm and the sensitivity control on the recorder. The sensitivity control is first used to obtain almost full-scale deflection on the recorder when the light is passing through the dye vessel (path B), and the iris diaphragm is then adjusted so that the same deflection on the galvanometer is obtained when light traverses the non-absorbing path (path A). When the dye vessel contains only water, losses due to reflection at the mirror surfaces and scattering at the windows and in the liquid are thus directly compensated. On the introduction of dye into the vessel the change in transmission in path B will be entirely due to the absorption of light by the dye molecules, and changes in the ratio $\log I_0/I$ will be directly proportional to the concentration of dye in the dyebath. The recorder is fitted with a synchronous clock, so the time taken for these changes in concentration to occur is also measured.

In experiments at constant dyebath concentration, the balancing operation is carried out with the required concentration of dye in the dyebath, and the magnitude of the signals obtained after balancing has no particular significance: all that is required is that signals derived from the two light paths should be kept equal. To enable this to be done, a trial calibration must be previously carried out at each dye concentration

TABLE I

Exhaustion of Naphthalene Red JS (C.I. Acid Red 88) on Nylon Yarn

Time (min.)	Recorder Readings A_1 (arbitrary units)	A_2	Optical Density of Dye in Bath $\left(\log \frac{A_1}{A_2}\right)$	Dye in Fibre $(D_0 - D_t)$ (arbitrary units)	Exhaustion of Bath (%)
0	92·0	45·0	0·311 = D_0	—	0
1	92·0	48·5	0·278 = D_t	0·033	10·6
2	92·0	53·0	0·239	0·072	23·1
4	92·2	57·5	0·205	0·106	34·0
8	91·3	64·0	0·154	0·157	50·5
16	89·7	70·5	0·105	0·206	67·2
32	87·2	75·0	0·065	0·246	79·0

to find the volume of dye that must be added to correct a small out-of-balance condition. Thus it might be found that 0·2 ml. of a particular solution was necessary to remove a difference between the signals from the two light paths of one division on the recorder chart. During an experiment the operator then watches for this out-of-balance condition to develop, and when it does, runs in from a burette the necessary amount of solution to restore balance, noting the time at which it is added. A graph of burette readings plotted against the time then shows the passage of dye from bath to fibre at a fixed bath concentration. The apparatus could alternatively be developed to operate some form of automatic titration process.

Examples of Use of the Meter

(1) As an example of the measurement of dyeing rates, Table I shows some results obtained when dyeing 1 g. of continuous-filament nylon yarn at 82·5°C. in a dyebath containing initially 0·02 g. Naphthalene Red JS, 3% acetic acid, 1% formic acid, and 1250 ml. water.

The second and third columns give values of A_1 and A_2 taken from the recorder chart after the dyeing had continued for the time given in the first column. These are proportional to the light intensities emerging from paths A and B respectively. The units are arbitrary, but since no adjustment to the apparatus is made once the balancing operation has been carried out, the factor of proportionality between I_0, I, and the photocurrent recorded on the chart will be constant at any time—

$$A_1 = \text{const} \times I_0$$
$$A_2 = \text{const} \times I \qquad \text{(i)}$$

The optical density of the solution in the dyebath at time t is given by—

$$D_t = \log \frac{I_0}{I} = \log \frac{A_1}{A_2} \qquad \text{(ii)}$$

so that, provided A_1 and A_2 are measured consecutively, changes in the value of the constant in equation (i) due to slow drifts in the intensity of the light source, sensitivity of the photomultiplier, or power supply voltage do not affect the results.

The fourth column in Table I gives the optical density of dye in the bath calculated on the basis of equation (ii). By subtracting from the initial optical density of the dyebath its value at time t, values of the concentration of dye in the fibre expressed in arbitrary units are obtained. The quantity of dye in the bath is known initially, so that the proportionality between the values of dye in fibre calculated by this method and the absolute values can be fixed if required.

TABLE II

Dyeing of Undrawn Terylene Yarn at 70°C. at Constant Concentration of 0·04 g. Chrysoidine YN (C.I. Basic Orange 2) in 1250 ml. Water

Dyeing Time t (min.)	$\sqrt{t}$	Dye Solution added (ml.) = Dye absorbed by Fibre (1 ml. = 0·4 mg. dye) Run 1	Run 2
2	1·41	4·5	4·2
4	2·00	6·0	6·0
8	2·82	9·0	8·8
16	4·00	12·6	12·8
32	5·66	17·9	18·8
64	8·00	25·8	26·3
128	11·31	37·4	39·1

(2) Dyeing with the dyebath concentration kept constant is illustrated by the results obtained with 5 g. undrawn Terylene yarn in a bath containing 0·04 g. Chrysoidine YN and 1250 ml. water at 70°C. The reproducibility can be seen from the results of the two separate experiments that are given (Table II). The linearity of the plot of dye in fibre against the square root of the time indicates that at this stage, when the fibre is ring-dyed, the course of the dyeing can be well approximated by the relation which holds for the diffusion of dye into a semi-infinite slab.

RESEARCH DEPARTMENT
IMPERIAL CHEMICAL INDUSTRIES LTD.
FIBRES DIVISION
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(*Received 11th September 1957*)

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The Effect of Sulphuric Acid on Wool
I—Influence of Concentration of Acid on the Histological Attack

R. L. ELLIOTT, R. S. ASQUITH, and D. H. RAWSON

The attack of sulphuric acid of various concentrations on wool has been examined under different conditions of temperature and time of treatment. The damaged fibres have been observed microscopically, and results correlated with weight changes and amide-nitrogen analyses.

The attack has been shown to be of the following main types—

(1) Hydrolysis in concentrations of acid up to 44% concentrated sulphuric acid by weight.

(2) Rapid dissolution in concentrations of acid between 44% and 81·3%, the histological attack being different from the simple hydrolytic attack in (1).

(3) A slow attack, at concentrations between 93% and 98%, which becomes considerably more rapid at temperatures above 60°C.

(4) A rapid oxidative attack and dissolution, presumably due to free sulphur trioxide, in acid concentrations above 98%.

At higher temperatures, all types of attack are more rapid.

INTRODUCTION

During recent years, numerous studies have been made of the attack of various reagents on the wool fibre. Thus Lindberg, Philip, and Gralén [1] endeavoured, by degradation of wool with sodium sulphide, to isolate the epicuticle postulated by Whewell and Woods [2]. Elöd and Zahn [3] isolated a "subcuticular" membrane by enzymatic treatment of supercontracted wool. Alexander and Earland [4] claimed isolation of the subcuticle membrane by peroxide oxidation followed by extraction with ammonium hydroxide. This work was later challenged by Fraser and Rogers [5], Gralén, Lagermalm, and Philip [6], and Elliott and Manogue [7].

Considerable work has also been published on the asymmetry of the cortex. Thus Horio and Kondo [8] showed that the cortex consisted of an outer, dye-accessible fraction and an inner, non-dye-accessible fraction. Mercer [9] simultaneously showed that these two fractions differed in their rates of digestion with enzymes, and that half the fibre, identical with the dye-accessible fraction, was more readily digested than the remainder. This fraction he termed the *orthocortex*, using the term *paracortex* for the non-dye-accessible fraction.

A mass of evidence has been accumulated showing a clear division of the cortex into segments [8–13]. All this work, however, has laid emphasis on the attempted isolation and identification of various components of the fibre, and few extensive studies have been carried out on the histological degradation of wool by simple reagents under standard conditions.

Elliott and Roberts [12] studied the progressive dissolution of wool with boiling 2 N. hydrochloric acid, and showed that dissolution occurred in three stages—(1) dissolution of 7% of the fibre, of indefinite histological significance; (2) dissolution of the orthocortex; and (3) gradual dissolution of the paracortex and a residual resistant membrane. No attempt was made, however, to study the effect of different concentrations of hydrochloric acid.

Although the treatment of wool with sulphuric acid is a common industrial process, the effect of this reagent, particularly at higher concentrations, has not been extensively studied from the aspect of histological degradation. Horio and Kondo [8] suggested from staining effects that 92–95% sulphuric acid at room temperature affects the non-dye-accessible fraction in preference to the dye-accessible fraction, whereas sulphuric acid at lower concentration has the reverse effect. Time of treatment, however, is not stated.

Thus the effect of different concentrations (0·25–102%) of sulphuric acid, under controlled conditions of temperature for various times of treatment, seemed worthy of investigation.

DISCUSSION

64s Merino wool, purified as described below, was used throughout this work. Basically three approaches were made to the problem—

(1) Microscopic examination

(2) Amide-nitrogen determination

(3) Weight-loss determinations on the wool.

The results of these three methods show considerable correlation.

Weighed samples of purified, dried wool were treated with different concentrations of sulphuric acid at 29°C. for 72 hr. The change in weight of the washed, dry wool was then determined. The results are shown in Fig. 1A.

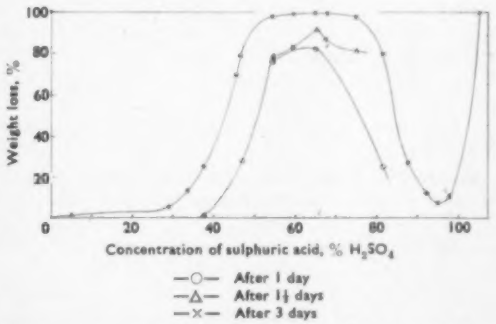

FIG. 1A—Weight Change plotted against Concentration of Sulphuric Acid at 29°C.

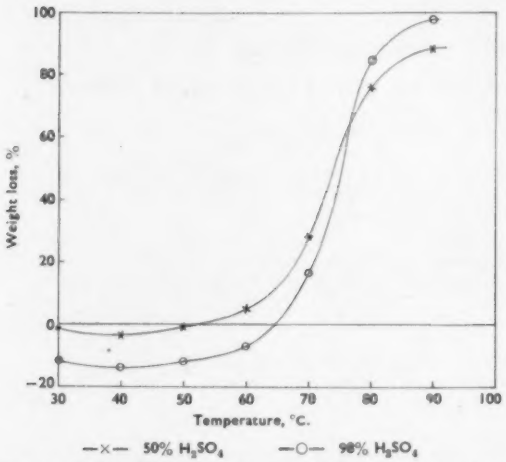

FIG. 1B—Weight Change after 15 min. plotted against Temperature

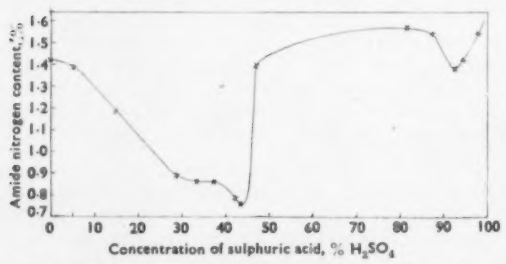

FIG. 2—Amide Nitrogen Content of Wool treated with various Concentrations of Sulphuric Acid for 72 hr.

Amide-nitrogen determinations were then carried out on the residual insoluble wool. The results are shown in Fig. 2.

At the same time, samples of wool immersed in the same concentrations of sulphuric acid (liquor ratio 100 : 1) were periodically removed, washed, stained with Methylene Blue (C.I. Basic Blue 9), and examined microscopically. The microscopy was carried out on wool treated at 29°C. and 90°C.

The weight changes indicate that the dissolution of the wool is relatively slow in concentrations of acid below 30% at 29°C., but the rate of dissolution increases gradually as the acid concentration increases. This is paralleled by a gradual fall in amide nitrogen content of the residual wool, which reaches a minimum at 43·4% acid. This fall in amide nitrogen is presumably due to hydrolysis of the free amide groups in the fibres, the extent of hydrolysis increasing with increasing acid concentration.

Samples of wool treated in the following concentrations of acid were examined microscopically — 0·25%, 0·5%, 1%, 4·9%, 19%, 28·8%, 37·5%, and 43·4% concentrated sulphuric acid by weight. The attack in concentrations below 19% at 29° and 90°C. was too slow to be of any practical interest. In acid concentrations of 19–43·4% the site of initial attack was uncertain, but prolonged attack in all these cases caused the residual fibres to become segmented (Fig. 3 and 4). In the final stages of attack, partially segmented tubular membranes were left (Fig. 5).

As the acid concentrations were increased above 43·4%, the rate of attack was much more rapid. Weight change determinations after 24 hr. acid treatment indicate that the maximum rate of attack is in 65% acid. Above 43·4% acid the results of amide nitrogen determinations show a sudden increase, which must presumably be due to some type of amino acid breakdown. Decomposition of arginine, first to citrulline and then, on hydrolysis, to ornithine, would account for the high amide nitrogen results[14]. It has been shown that arginine partially decomposes to citrulline and ornithine with concentrated sulphuric acid. Any citrulline so formed during concentrated acid treatment would, at a later stage, on hydrolysis of damaged wool, be decomposed to ornithine with consequent liberation of ammonia.

A sample of wool which had been treated with 44·5% acid was filtered off from the acid. The filtrate, after removal of inorganic ions, was examined by two-dimensional chromatography by the techniques given below. The chromatogram showed the constituents of the filtrate to be mainly amino acids together with a little peptide material. This indicates that the attack is mainly hydrolytic under these conditions.

Samples of wool treated with the same concentrations of acid as for the weight changes, viz. 44·5%, 46·7%, 54·5%, and 59·3%, were examined after staining with Methylene Blue as indicated above.

The most notable feature of the attack by acids of these concentrations was the swelling of a scale-marked membrane round the residual fibres (Fig. 7). The cortex slowly dissolved from within the swollen membrane, which was obtained free from other material after 6 days in 46·7% acid at 29°C. (Fig. 8). In 59·3% acid at 90°C. the initial attack was on the scales (Fig. 6), and the membrane described above was not as apparent; 10 min. attack under these conditions left the cortex free from other components (Fig. 9).

As the acid concentration was increased above 65%, the attack became slower. The amide nitrogen values remained high and the type of attack as observed microscopically in concentrations up to 81·3% at 29° and 90°C. was similar to that in 44·5–65% acid. The scale-marked membrane was less apparent, and, as the acid concentration increased, was more readily attacked than the cortex. Rising temperature also caused damage to the membrane in preference to the cortex.

As the acid concentration increased (94·8–98%), the rate of attack became slower, the weight-change curve showing a minimum at 94·8%. Amide nitrogen values remained high in this region, but the type of attack was different. In these concentrations, areas of scaly material were rapidly attacked and split from the fibres (Fig. 10), after which further attack was much slower. After 10 days' treatment in these concentrations the wool was still fibrous and appeared to have

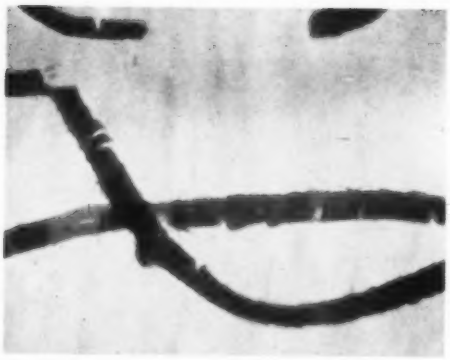

FIG. 3— Wool treated with 19% H_2SO_4 for 4½ hr. at 90°C. (× 256) showing Fibre Segmentation

FIG. 4— Wool treated with 43·4% H_2SO_4 for 7 days at 29°C. (× 300) showing Segmentation of the Cortex

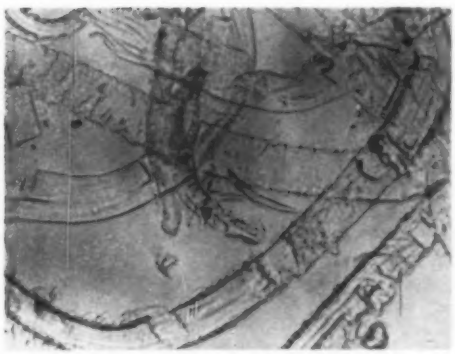

FIG. 5— Wool treated with 28·8% H_2SO_4 for 2 hr. at 90°C. (× 300) showing Segmentation and Residual Tubular Membranes

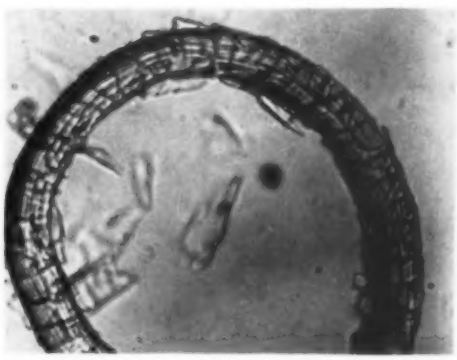

FIG. 6— Wool treated with 59·3% H_2SO_4 for 2 min. at 90°C. (× 300) showing Scales splitting from Fibres

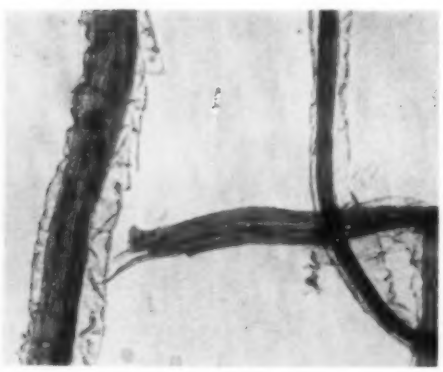

FIG. 7— Wool treated with 44·5% H_2SO_4 for 4 days at 29°C. (× 300) showing a Scale-marked Membrane swollen round the Cortex

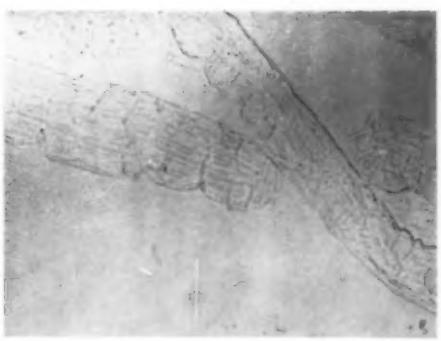

FIG. 8— Wool treated with 46·7% H_2SO_4 for 6 days at 29°C. (× 300) showing Residual Membrane

Note— Samples in Fig. 3–12 have been stained with Methylene Blue stain. Those in Fig. 13 and 14 have been stained with Pauly reagent.

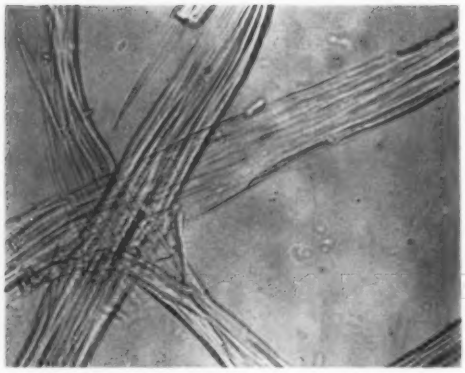

FIG. 9— Wool treated with 59·3% H_2SO_4 for 10 min. at 90°c. (× 300) showing Cortices denuded of other Histological Components

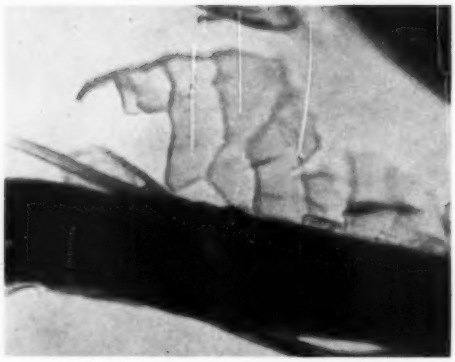

FIG. 10— Wool treated with 98% H_2SO_4 at 29°c. for 20 min. (× 500) showing Scales splitting from the Fibres

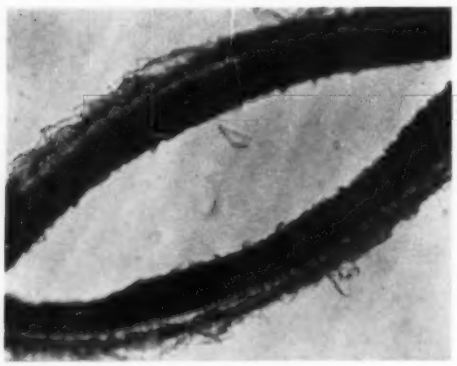

FIG. 11— Wool treated with 94·8% H_2SO_4 for 4 days at 29°c. (× 300) showing Differential Staining

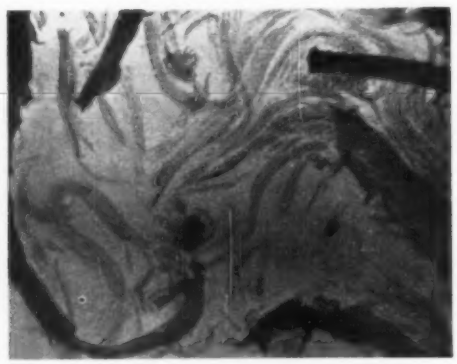

FIG. 12— Wool treated with 102% H_2SO_4 for 15 min. at 29°c. (× 110) showing Fibre Decomposition into Bundles of Cortical Cells

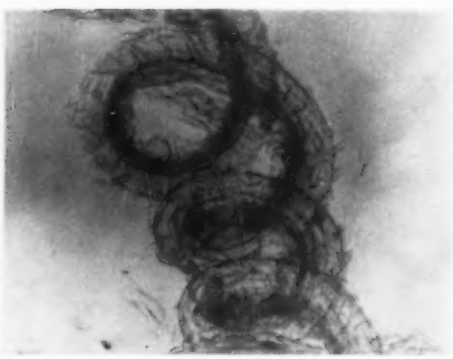

FIG. 13— Wool treated with 98% H_2SO_4 for 4 days at 29°c. after Pauly Staining

FIG. 14— As Fig. 13 after compressing with Microscope Cover-slip

suffered little further damage. The fibres were stained differentially (Fig. 11), and, although the inside of the curved fibres was heavily stained, this portion appeared to be less heavily damaged than the outer segment of the cortex. Staining is discussed more fully below.

A sample of wool which had been treated with 94·8% acid for 3 days was filtered off from the acid, and the filtrate, after removal of inorganic ions, was examined by two-dimensional chromatography, the techniques being given below. The chromatogram showed the constituents of the filtrate to be mainly peptides, indicating that the type of attack was dissolution rather than hydrolysis.

The rate of attack by acid concentrations above 98% was very rapid, presumably owing to oxidation of the cystine links by free sulphur trioxide. Microscopically the attack was seen first on the scales, which split from the fibres and dissolved. The cortex then broke down completely within 15 min. to give bundles of cortical cells (Fig. 12). Wool (0·5 g.) was treated with 50 ml. of 102% sulphuric acid (i.e. 2% oleum). Complete solution had occurred after 20 min. The protein material was hydrolysed by diluting to 500 ml. and boiling under reflux. The resulting solution, after removal of inorganic ions, was examined by two-dimensional chromatography. The chromatograms showed the presence of cysteic acid, indicating that oxidation is the primary cause of attack.

Weight changes were also measured on wool which had been treated with 50% and 98% acid for 15 min. at different temperatures (Fig. 1B). Both of these acid concentrations caused an increase in weight of the wool sample up to a maximum at 40°C.

This initial weight gain is in agreement with the findings of Harris, Mease, and Rutherford [15], who showed that 80% sulphuric acid at 25°C. reacted chemically with wool, producing a maximum increase in weight of 7·19% after 30 min. treatment. They suggested that this was due to the following reaction with basic side-chains in the wool—

$$R{\cdot}NH_2 + H_2SO_4 = R{\cdot}NH{\cdot}SO_3H + H_2O$$

The chemistry of this attack will be further discussed in Part II.

Many anomalies were observed in the staining of the wool samples with Methylene Blue, prior to microscopic examination, and it is difficult to correlate staining with acid concentration or time of treatment. Various points connected with staining are, however, worthy of note. In many cases staining after initial stages of acid attack was heavy, but after prolonged treatment no staining was observed.

Fibres attacked by 98% sulphuric acid were heavily stained in the first instance (Fig. 10), but after prolonged treatment differential staining was apparent (Fig. 11). The outside of curved fibres appeared microscopically to have suffered the greatest amount of damage, although these outer segments of the fibres were completely unstained (Fig. 11).

Horio and Kondo [8] state that strong acid affects the non-dye-accessible fraction (paracortex) in preference to the outside segment of the fibre. Assuming that no irregular twisting of the fibres has occurred, this statement does not agree with current observations that the outside of the curved fibres (orthocortex) is most readily attacked. Methylene Blue staining is therefore an unreliable test of very heavy chemical attack on wool fibres.

A sample of wool treated for 4 days with 98% sulphuric acid was stained with Pauly reagent. This caused extensive coiling and dissolution of the fibres to leave a coiled membrane (Fig. 13). This membrane was easily broken by compression of the cover slip (Fig. 14).

It is possible that anomalies in Methylene Blue staining may be caused by varying amounts of free sulphuric acid remaining in the fibres after washing, but further investigation is necessary for verification of this suggestion.

EXPERIMENTAL

(1) *Preparation of Raw Wool*

Wool tips were removed from 64s Merino wool, which was then degreased by Soxhlet extraction overnight with ether, and then alcohol. The wool was air-dried, and burrs were removed by hand. The wool was washed in running water for 24 hr., and then dried. Samples for microscopic examination and weight-change determinations were dried for 4 hr. at 100°C. before use.

(2) *Weight Changes*

Dried wool (0·5 g.) was treated with 50 ml. of the appropriate acid concentration for the required time. The wool was then filtered off through a tared No. 1 sintered-glass crucible, and washed with ether and then acetone; finally water was allowed to run through slowly for 30 min. The crucible and the sample were dried for 4 hr. at 120°C. and reweighed.

(3) *Staining*

Samples of wool (each 0·5 g.) were treated with 50 ml. of acid of the appropriate concentration and temperature. Samples were withdrawn at intervals and after washing with ether, acetone, and water were stained by treating with 0·5 ml. of 0·004 M. Methylene Blue solution buffered at pH 7 [16]. The samples were mounted in water and examined microscopically.

(4) *Amide Nitrogen Estimation*

The wool samples isolated in the weight-change determination were used for amide nitrogen estimations. A weighed amount of the sample was refluxed with 5 ml. of 6 N. hydrochloric acid for 5 hr. and made up to volume. Aliquots were withdrawn and run into the micro-Kjeldahl apparatus of Parnas and Wagner. After adding sufficient 40% caustic soda solution for neutralisation, the sample was steam-distilled, and the ammonia absorbed into saturated boric acid solution. The ammonium borate was titrated with 0·0105 N. hydrochloric acid using a mixed indicator of Bromocresol Green and Methyl Red.

(5) *Chromatography*

Chromatograms were run in Shandon cabinets and were of the descending type. The solvents

used for two-dimensional chromatography were—

(i) Butanol–acetic acid–water in the proportions 4 : 1 : 5. The upper layer was used for elution of the paper, and the lower layer to give the atmosphere in the tanks.

(ii) A phenol–water mixture was made up as follows— 500 g. of phenol was melted, and water was added to the fused phenol until the mixture became cloudy. A solution of phenol containing a little water was added, after cooling, until a clear solution was obtained. 8-Hydroxyquinoline (0·1 g.) was added, and coal gas was passed through for 1 hr. The one-phase system obtained was used as eluting agent and also to provide the atmosphere in the tank.

Chromatograms were run on Whatman No. 1 24 cm. × 24 cm. paper. All chromatograms were dried after elution by allowing them to stand overnight in the atmosphere and developed by spraying with a 0·2% solution of ninhydrin in acetone, and heating to 70°C. for 5 min.

Sulphuric acid solutions for chromatographic examination were neutralised with barium hydroxide solution, excess barium being precipitated with carbon dioxide. After filtration, the solutions were concentrated under reduced pressure.

CONCLUSIONS

From the above evidence it appears that the mechanism of attack on wool by sulphuric acid is basically of the same type at 29°C. and at 90°C.

In acid concentrations up to 43·4%, amide nitrogen analyses indicate that the mechanism of attack is a general hydrolysis, which is accompanied, in the later stages of attack, by segmentation of the fibres, as observed microscopically.

In acid concentrations of 43·3–81·3%, rapid solution occurs, but the histological attack is different from the simple hydrolytic attack in the above concentrations; no segmentation is observed. A change in mechanism of attack is supported by a sudden increase in amide nitrogen content of acid-treated fibres. This increase is consistent with amino acid breakdown, and it is probable that conversion of arginine, first to citrulline and then, on subsequent hydrolysis, to ornithine, contributes to the high values. The maximum rate of attack is in 65% acid.

Acid of concentration 90–98% on wool, after removal of the scales, appears slowly to dissolve wool substance. A type of attack involving dissolution is supported by chromatographic examination, which indicates the presence of considerable quantities of peptide material in the acid used.

In 102% acid, wool is attacked primarily by a process of oxidation, since cysteic acid is present in the solution of wool obtained in this strength of acid, as indicated by chromatography.

The attack of 98% acid shows certain features outside the scope of this paper. Results of further investigations on the effect of this reagent on wool follow.

* * *

The authors are indebted to the Wool Textile Research Council for permission to publish this work, and for a grant to one of us (D.H.R.).

DEPARTMENT OF CHEMISTRY AND DYEING
BRADFORD INSTITUTE OF TECHNOLOGY
BRADFORD 7
YORKSHIRE

(*Received 26th September 1957*)

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The Effect of Sulphuric Acid on Wool
II—The Chemical Attack of Concentrated Acid

R. L. ELLIOTT, R. S. ASQUITH, and D. H. RAWSON

Investigation of wool samples after various times of treatment with concentrated sulphuric acid has shown that hydrolysable sulphate increases to a maximum after 1 hr. A fall in sulphate after 1 day to a relatively constant value corresponds to the loss of a scaly membrane. A slow increase in total sulphur is due to removal of the low-cystine-containing fraction of the fibre and to slow benzene-ring sulphonation.

Hydrolysates of wool treated with sulphuric acid contain substances identical with those produced on sulphonation of amino acids. Histological changes observed microscopically agree with the results of chemical analysis.

Introduction

Much work on the chemical reaction between concentrated sulphuric acid and wool was carried out by Harris, Mease, and Rutherford [1]. These workers found that, on treating wool with 80% sulphuric acid, combined sulphur was introduced into the fibres. This sulphur could be estimated by its easy hydrolysis to free sulphate. The increase in weight and the sulphate content could be accounted for by sulphation of some reactive groups. These authors found that the maximum increase in sulphate content, viz. 8·38%, occurred

after 30 min. treatment at 25°C., giving a weight increase of the fibre of 7·19%. On the basis of this work, they suggested that the acid had reacted with amino side-chains in the wool to give sulphamic acid derivatives—

$$R{\cdot}NH_2 + H_2SO_4 = R{\cdot}NH{\cdot}SO_3H + H_2O$$

Assuming that all these side-chains react, we have calculated that the maximum increase in weight would be 6·6%, using the most probable amino acid content values of Harris[2].

Speakman[3] also indicated that tyrosine side-chains were sulphonated in the benzene ring; such a reaction, however, presumably would not give an easily hydrolysable product, but would account for the additional weight increase.

Lustig and Kondritzer[4] investigated the effect of concentrated sulphuric acid on red hair at 0°C. for 24 hr. and found that, after treatment, the hair contained a reduced content of serine, tryptophan, tyrosine, phenylalanine, and arginine. This reaction must therefore be more complex than simple sulphamic acid formation. The latter authors suggested that sulphonation of amino acids containing benzene rings may be partly responsible for the increase in sulphur content of the fibres, in support of Speakman's previous suggestion.

Reitz *et al.*[5] suggested that sulphuric acid at 0°C. brought about mainly sulphation of the aliphatic hydroxy groups of serine in a number of proteins including wool, and that other reactions were of secondary importance. In a similar type of reaction Ferrel *et al.*[6] indicated that the hydroxy groups of serine in proteins could be phosphorylated with phosphoric anhydride in phosphoric acid, when the reaction is confined almost entirely to serine.

Elliott, Asquith, and Rawson[7] showed that the only types of attack which occurred on free amino acids were sulphation of hydroxy groups and sulphonation of benzene-ring side-chains as in tyrosine and phenylalanine. No attack appeared to occur on amino groups of free amino acids, and therefore the Reitz suggestion of sulphation of hydroxy groups seemed more probable than the Harris theory. The present work strongly supports the former theory of Reitz, viz. sulphation of hydroxy groups and sulphonation of benzene rings.

Discussion

64s Merino wool, purified as described below, was used throughout these investigations. An examination of the effect of concentrated sulphuric acid on wool was carried out using the following methods— microscopic examination, chemical analysis (amide nitrogen, sulphur, sulphate, and cystine), weight changes, and chromatographic examination.

Considerable correlation was observed in the results obtained by these various methods.

1. MICROSCOPIC EXAMINATION

Samples (each 0·5 g.) of wool were treated with 50 ml. concentrated sulphuric acid at 29°C. using a liquor ratio of 100 : 1. Small samples were withdrawn, washed as indicated in Part I (previous paper), and examined microscopically.

The fibres swelled rapidly to a jelly-like mass, but on washing retained their fibrous structure throughout the treatment. After 20 min., areas of scaly membrane began to split from the fibres, which subsequently stained heavily and uniformly with Methylene Blue under the standard conditions (Fig. 10, Part I). After 1 day most of this membrane had dissolved. After 2 days the type of staining changed and differential staining occurred. The inside segment of curved fibres (paracortex) was heavily stained, while the outer part (orthocortex) was not. Assuming that no unusual twisting of the fibres had occurred, it was observed microscopically that the orthocortex of the fibres was more heavily damaged, but, paradoxically, this was the segment of the fibres which was least heavily stained. This has been considered in the previous paper.

After this stage the fibre appearance then remained the same until the 14th day, when the fibres began to split into short lengths.

After 4 days' treatment, a sample of wool was stained with Pauly reagent, when extensive coiling of the fibres occurred. Most of the fibres dissolved in this alkaline reagent, leaving a coiled membrane which was easily broken down by compressing the microscope cover-slip. A thin layer of stained paracortex remained undissolved within the tubular membrane. Presumably, this residual paracortex was responsible for the coiling of the tubes in microscopic ringlets (see previous paper, Fig. 13).

2. CHEMICAL ANALYSIS

Samples of wool were treated with concentrated sulphuric acid under the conditions given below, and after washing and drying were used for sulphur, sulphate, amide nitrogen, and cystine estimations. The results are given in Table I.

The percentage combined sulphur and cystine fall to a minimum after 1–2 hr. This is presumably connected with the breaking away and dissolution of the scaly membrane as observed microscopically. Analyses show that the cystine content of the fibre diminishes in this time. This would be consistent with some part of the dissolving cuticle having a high cystine content, in agreement with the conclusion of Geiger[8], and of Elliott and Roberts[9], that the epicuticle had a high cystine content.

During the first 2 days' treatment, while a certain amount of cuticle remains undissolved, there is a high proportion of free sulphate in the sulphuric-acid-treated wool. This free sulphate content falls off markedly as the cuticle sheath dissolves. Sulphation of all the hydroxyl groups of serine and threonine in wool would give a calculated value of 12·2% free sulphate, whereas the maximum observed sulphate value is 10·65%. Allowing for some hydrolysis of unstable sulphates during washing processes, these values are reasonably close. If all the free sulphate is formed from the reactive hydroxyl groups of serine and threonine, at least one half of these amino-acid residues must be present in the cuticle, to account for the fall in

TABLE I

Time	S (%)	SO_4 (%)	S in SO_4 (%)	Cystine (%)	S in Cystine (%)	Fixed S (%)
0 min.	3·86	—	—	11·4	3·04	0·82
10 min.	7·44	10·65	3·55	10·5	2·8	1·09
1 hr.	7·05	10·30	3·43	—	—	—
2 hr.	6·69	9·16	3·05	10·1	2·69	0·95
3 hr.	7·25	8·25	2·75	10·4	2·77	1·73
1 day	7·30	5·30	1·76	10·3	2·75	2·79
2 days	7·65	4·55	1·52	12·2	3·26	2·87
4 days	7·74	4·43	1·48	13·8	3·68	2·58
7 days	8·74	4·27	1·42	13·8	3·68	3·65

free sulphate content from 10·65% to 5·30% on dissolution of the cuticle sheath. The maximum value obtained for hydrolysable sulphate by Harris, Mease, and Rutherford [1], using 80% sulphuric acid, was 8·38%. Both this value, and the present maximum of 10·65%, are considerably higher than would be obtained if the sulphate groups were bound by basic side-chains. Assuming that all the basic side-chains of arginine and lysine are sulphated, this would give rise to a hydrolysable sulphate content of 7·41%.

The results of present work can be interpreted in one of the following ways: the dissolving cuticle sheath consists of either— (1) at least two membranes, one of which has a high cystine content and the other of which is polysaccharide in nature, giving rise to a considerable number of sulphated hydroxyl groups other than hydroxyamino acids (this supports the evidence of Lagermalm and Gralén [10] for the existence of an epicuticle sheath which is polysaccharide in nature); or (2) a single membrane which contains a high proportion of cystine and hydroxyamino acids, the latter conferring solubility by sulphation, despite the cystine cross-links.

The results obtained, however, are insufficient to indicate any clear conclusions, and further work is necessary before the nature of the dissolving material can be established with certainty.

Combined sulphur, other than cystine and sulphate sulphur, has been obtained by subtracting the figures for cystine and sulphate sulphur from the figure for total sulphur. In virgin wool this residual sulphur (0·8%) will presumably be due partly to methionine plus traces of cysteic acid and lanthionine. This figure, however, is too high to be explained as solely due to these acids, but is in agreement with the results of Phillips and Cuthbertson [11], who obtained a value of 0·9%.

As the time of treatment increases, the value for this figure increases considerably. This slow increase in fixed sulphur is consistent with a slow sulphonation reaction of the benzene ring in tyrosine, in agreement with Speakman [3], and also in phenylalanine.

After the initial fall, the slow increase in cystine content with time is to be expected, as a phase containing few cystine cross-links should be more readily attacked, leaving a residue higher in cystine content, presumably the tubular membrane referred to in the previous paper.

The amide nitrogen analyses were variable, and were often higher than the figure for virgin wool. If any form of hydrolysis or breakdown of amide groups occurs, a fall in amide nitrogen due to hydrolysis to ammonia could be expected (as in lower concentrations). Possibly, any such breakdown is counterbalanced by the conversion of arginine to citrulline. This slow decomposition of arginine has already been shown to occur [7]. The citrulline then yields ammonia on analytical hydrolysis, decomposing to give ornithine and causing variation in the amount of amide nitrogen estimated, so that a figure higher than that for virgin wool would then be possible.

3. WEIGHT CHANGE

Weight-change determinations were carried out, and the results obtained are shown in Table II.

TABLE II

Time	Weight Gain (%)
30 min.	9·4
1 hr.	9·9
3 hr.	11·5
1 day	2·3
2 days	−3·7
4 days	−22·0
7 days	−38·1

The initial weight gain can be accounted for by the increase in free sulphate: 10·5% free sulphate would cause a calculated weight gain of 11·7%. This weight gain is offset after 2 days by the slow dissolution of the fibres.

4. CHROMATOGRAPHIC EXAMINATION

After hydrolysis with 4 N. sulphuric acid and removal of inorganic ions, solutions of hydrolysed normal wool and hydrolysed wool which had previously been treated with sulphuric acid (98%) for 7 days were fractionated electrophoretically into acidic, basic, and neutral fractions (see *Experimental*).

(*a*) *Acidic Fractions*

The acidic fractions of wool and sulphuric-acid-treated wool were run chromatographically, against controls of sulphuric-acid-treated serine, sulphuric-acid-treated tyrosine, sulphuric-acid-treated phenylalanine, and untreated aspartic and glutamic acids, for 64 hr. in butanol–acetic acid–water solvent. Under these conditions the acid spots travelled a considerable distance down the paper.

The acidic fractions of hydrolysates of normal wool and sulphuric-acid-treated wool both contained aspartic and glutamic acids, but the sulphuric-acid-treated wool hydrolysate contained four

additional spots. One of these was identical with the major spot from sulphuric-acid-treated tyrosine. The other three spots had approximately the same R_f values as the products of the action of sulphuric acid on phenylalanine, but their identity could not be established with certainty, since both sulphuric-acid-treated serine and sulphuric-acid-treated tyrosine gave spots in this region, although the serine sulphate would not be expected to survive hydrolysis. The fractions were, therefore, submitted to two-dimensional chromatography, and were run against controls of sulphuric-acid-treated tyrosine and sulphuric-acid-treated phenylalanine. The acidic fraction of the hydrolysate of sulphuric-acid-treated wool contained three additional spots. One of these corresponded to one of the spots from acid-treated phenylalanine and another to the major spot of acid-treated tyrosine ($R_f = 0$). The identity of the third spot is uncertain, since subsidiary spots in acid-treated phenylalanine and tyrosine have approximately the same R_f values. The fourth spot was not detected on the two-dimensional chromatogram, presumably because of its low concentration.

These apparently hitherto unknown amino acid derivatives are identical with those obtained by the action of sulphuric acid on amino acids and have been shown to be aromatic amino acids sulphonated in the benzene ring [7]. This supports the evidence of Lustig and Kondritzer [4], who found a reduction in the tyrosine and phenylalanine contents in red hair after treatment at 0°C. with concentrated sulphuric acid for 24 hr. It is also in agreement with the findings of Speakman [3], who showed that tyrosine side-chains of wool are sulphonated by concentrated sulphuric acid.

(b) *Neutral Fraction*

A one-dimensional chromatogram was run of the neutral fraction of hydrolysed wool and sulphuric-acid-treated wool in butanol – acetic acid – water solvent. The resulting chromatograms were identical, except that the fraction from acid-treated wool contained no tyrosine at all and only a small phenylalanine spot. This supports the view that ring sulphonation of these acids has occurred to a considerable extent.

(c) *Basic Fractions*

Examination of the basic fractions of hydrolysed wool and sulphuric-acid-treated wool by one-dimensional chromatography in butanol–acetic acid–water solvent did not give full separation of the basic amino acids. A further run in phenol–water solvent in an acetic acid atmosphere (Dent [12]) showed that the fraction from acid-treated wool contained a small quantity of ornithine in addition to the usual acids.

Experimental

1. CHEMICAL ANALYSIS

(a) *Treatment of Samples*

Dried wool (2 g.) was put into 200 ml. of 98% sulphuric acid at 29°C. for the appropriate time. The wool was filtered off, washed with 100 ml. of ether for 15 min., 100 ml. of acetone for 15 min., and running water for 2 hr. The samples were then filtered off, and dried in an oven overnight at 100°C. These samples were used for sulphur, sulphate, amide nitrogen, and cystine estimations, the methods being given below.

(b) *Sulphur Estimation*

Wool samples were oxidised with boiling nitric acid and made up to volume, and aliquots were evaporated to dryness with Benedict–Dennis reagent. The residue was taken up in 6 N. hydrochloric acid, and the sulphate precipitated with 10% barium chloride solution.

(c) *Free-sulphate Analyses*

Samples were refluxed with 6 N. hydrochloric acid for 6 hr. The solution was made up to volume, and aliquots were withdrawn and diluted. Free sulphate was precipitated with 10% barium chloride solution at the boil.

(d) *Amide Nitrogen Analyses*

See Part I (previous paper).

(e) *Cystine Analyses*

Wool samples were refluxed with 20 ml. of 6 N. hydrochloric acid for 4 hr., filtered, and made up to volume. This solution (2 ml.) was taken, and the cystine estimated colorimetrically by means of phosphotungstic acid reagent, on a Unicam SP 601 spectrophotometer.

(f) *Weight Changes*

See Part I.

2. ELECTROPHORESIS

Electrophoretic separation of the amino acid fractions of wool was carried out in an EEL X118 electrophoresis apparatus using a borate buffer and Whatman No. 1 filter paper. A strip of paper containing a control of the same solution was run alongside the main electrophoretic run. The control was dried and developed with ninhydrin, when three bands, corresponding to the acidic, basic, and neutral groups of amino acids, were obtained. This was used as a template, and the fractions were cut from the main runs. The amino acids of the various fractions were extracted from the paper by pushing the rolled paper down a semi-micro condenser and refluxing 5 ml. of water continuously over the paper. The solutions were concentrated and applied directly to the chromatograms.

3. CHROMATOGRAPHY

Chromatography was carried out on Whatman No. 1 filter paper sheets 24 in. × 24 in., the solvents being (i) butanol–acetic acid–water (4 : 1 : 5) and (ii) phenol–water mixture. For the preparation of these solvents see Part I.

One-dimensional chromatograms were usually run in the first solvent. Two-dimensional chromatograms were run in (i) until the solvent front was within 2 in. of the bottom edge of the paper. The paper was then removed and allowed to air-dry overnight. It was then turned at right

angles and run in solvent (ii), after which it was removed and allowed to air-dry overnight.

All chromatograms were developed by spraying with a 0·2% solution of ninhydrin in acetone, and heating to 70°C. for 5 min.

Samples of wool used for chromatographic examination were (i) virgin wool and (ii) wool treated with sulphuric acid for 7 days and isolated as described under § 1 (*a*).

Samples (i) and (ii) were hydrolysed with 4 N. sulphuric acid for 4 hr. The sulphuric acid was then precipitated with barium hydroxide solution, excess barium being removed by passing carbon dioxide through the solution. After filtration, the solution was concentrated, and then applied directly to the chromatograms.

Conclusions

Correlation of chemical, microscopic, and chromatographic data obtained from the action of concentrated sulphuric acid on wool shows that the attack is made first of all on the cuticle, and indicates the presence of a considerable number of free hydroxy groups, which may be due to serine and threonine residues in the cuticle or to the presence of molecules which are polysaccharide in nature.

After removal of the cuticle sheath, a progressive dissolution of the fibre occurs, which is accompanied by slow sulphonation of the amino acids containing benzene rings.

* * *

The authors are indebted to the Wool Textile Research Council for permission to publish this work and for a grant to one of us (D.H.R.).

DEPARTMENT OF CHEMISTRY AND DYEING
BRADFORD INSTITUTE OF TECHNOLOGY
BRADFORD 7
YORKSHIRE

(*Received 26th September 1957*)

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The Pad–Jig System of applying Vat Dyes to Linen Cloth

J. N. F. PHILLIPS

A practical description is given of a system of dyeing linen cloth with vat dyes by the pad–jig method, employed in a dyehouse whose annual production exceeds two million yards (for dresses and shirts). Stress is laid on the attainment of the highest possible absorbency during bleaching and other preparatory treatments for dyeing. Details of the padding mangles are given, and the danger of aggregation of dye as a result of the use of unsuitable padding oils is discussed.

This paper is concerned only with fabrics prepared from long-line (wet-spun) linen yarn, which is made up of the long fibres remaining after elimination of the tow, which is used for the production of dry-spun yarns.

Linen is a hard fibre; it is easily damaged chemically and mechanically, so that greater care in handling and weaker solutions of the various chemicals used in bleaching are necessary than with cotton. Moreover, it is not subjected to high-pressure kier boils. Bleaching is quicker today than it was when the writer first entered the industry: the use of caustic soda, sodium and hydrogen peroxides, and, more recently, sodium chlorite have cut down the time quite considerably. Comparison with the old system of lime boils, scalds, the use of dunters* and rub-boards is outside the scope of this article. Incidentally, the writer is fortunate in possessing a number of samples of linen, plain and drill, bleached and finished in Northern Ireland more than 100 years ago, which, today, are still perfectly white. One of the reasons for weaker solutions, sometimes forgotten, is that too drastic treatment can cause linen to lose its natural sheen, which cannot be recovered.

* A series of giant wooden hammers that rise and fall, thus beating ("dunting") the wet cloth.

Linen cloth intended for dyeing is usually woven from bleached yarn, and tests should be carried out regularly in order to detect overbleaching. Solubility-number tests and microscopical tests using sodium zincate as a swelling agent are useful. With practice, the sodium zincate test will provide information whether any damage suffered has been caused by acid, alkali, or bacteria or by mechanical action.

Singeing is the first operation, and may be carried out on plate, gas, or combined plate and gas singeing machines. Care should be taken that the cloth is evenly singed from selvedge to selvedge, as faults here will show up after dyeing. These can, at times, be very difficult to identify as having been caused by the singeing machine. During the preparation of the cloth for dyeing, creasing or rubbing during wet-treatments should be guarded against. Crease marks so formed will show up in the finished piece.

Mercerising or caustic shrinking may be carried out either before or after bleaching and dyeing, the choice depending largely on the finish required and the characteristics of the vat dyes used. Cloth intended for a crease-resist finish is bleached, vat-dyed, and then mercerised. This method has been found to give a cloth with a fuller and softer

handle than when mercerising is carried out before bleaching. Cloth to be finished white is mercerised before bleaching because of the tendency to become slightly yellow after mercerising. With a few vat dyes— which change too much in hue or depth— it has been found necessary to dye on mercerised cloth in order to avoid matching to shade. Even though all the vat dyes in use have been carefully selected for this work, there are some colours that can be produced only with dyes having somewhat inferior fastness properties. For the purpose of mercerising, various types of plant are in use, e.g. the normal mercerising range, the so called linen merceriser, which does not have a stenter section, and jigs. Good results can be obtained by any of these arrangements, width control being easiest to attain with the mercerising range. When the caustic soda treatment is carried out before bleaching, the writer's practice is to leave, by means of controlled washing, sufficient caustic soda in the cloth for the scouring treatment.

Cloth made from dressed yarn is preferably desized before mercerising in order to prevent the caustic soda from becoming dirty and contaminated with size. The desizing treatment should be as effective as possible. One of the newer types of desizing agent used in the scouring bath has given excellent results in the writer's practice.

The scouring treatment must be thorough, and is carried out in fully enclosed stainless-steel winces. After scouring, the cloth is first washed free from alkali with hot water and finally with cold water. The cloth is next soured, washed thoroughly, and bleached with hydrogen peroxide.

The degree of bleaching necessary is a point on which there does not appear to be any general agreement. Many people consider that it is unnecessary to bleach to as high a degree of whiteness for deep colours as for medium and pale colours. The writer's practice, after an extensive series of laboratory and works tests, is to bleach all linen cloth to a certain standard, irrespective of the depth of colour that may be required subsequently. The advantages, especially in a vertical firm, are obvious.

During preparation for dyeing, every treatment should have, as its aim, the attainment of the highest possible degree of absorbency. The dyer is not assisted in getting a high degree of penetration if the cloth he receives from the bleach-house is beautifully white, but requires 30 sec. or more for a drop of water to diffuse through it. Imbibition and solubility-number tests should therefore be carried out regularly.

The solubility number has been mentioned before and, to prevent possible confusion in the minds of those more conversant with cuprammonium fluidity, it may be stated that these two tests fulfil a similar purpose, viz. determination of the degree of degradation suffered by the cloth or fibre. The cuprammonium fluidity test can be applied to linen, but, owing to the presence of substances insoluble in "cuprammonia", filtering is necessary. This filtering requires rather elaborate precautions if loss of ammonia and oxidation of the cellulose solution by air are to be prevented. The method of estimating the solubility number does not call for other than normal exactness in laboratory technique. It is, in effect, the estimation of the amount of cellulose dissolved in cold concentrated caustic soda solution (10 N.) afterwards diluted to 2 N. The amount so dissolved when calculated as a percentage of the original weight of material is the solubility number. The higher this number, the greater the degree of degradation. Expressed simply, a solubility number of 8 means that 8% of the material was removed by the cold concentrated caustic soda solution. The method described by Nodder[1] is very useful for normal routine work and is the method used by the writer.

A very large percentage of bleached and dyed, etc. linen cloth is finished to ensure crease-resistance. Hence, a very strict control is exercised in the bleach-house in order to obtain a cloth with a solubility number not exceeding 5·5. In the works with which the writer is associated, the aim is to produce a finished cloth with a solubility number not greater than 7.

The imbibition test is made on a centrifuge of 2,000 r.p.m., holding two tubes, the distance between the ends of the tubes being about 12 in. It is essential that the operating conditions be kept constant in order to obtain reproducible results. Normally, several estimations are made on each lot of cloth, and a figure of 62% is obtained on well prepared linen cloths with the centrifuge in use.

Absorbency tests easily and rapidly carried out are— (*a*) A small piece of the cloth (½ in. square) is dropped on to cold water contained in a beaker. If thoroughly bottomed, the sample will sink in about 3 sec. It is advisable not to touch the samples with the fingers in order to prevent possible contamination from perspiration, the use of forceps being recommended. (*b*) A drop of water from a pipette or dropping bottle is floated on to the surface of the cloth, held in a pair of common embroidery hoops. If the cloth has been properly bottomed, the drop will sink rapidly into the cloth and spread evenly on both warp and weft in 2–3 sec. The water used in these tests is the normal works supply, which is softened to zero hardness.

After bleaching, the cloth is dried on a stenter frame to an even width, cooled, and batched in lengths suitable for dyeing.

PADDING MANGLES

Four padding mangles are in use by the writer, varying from 50 in. to 72 in. wide (effective width of bowls). All follow the same arrangement of bowls, viz. soft, hard, soft. Two of these padding mangles have the pressure applied in a not very common manner: the pressure is applied to both top and bottom bowls independently of each other, so that conversion to two-bowl working can be effected in a few seconds. On these two machines the pressure source is compressed air; they have a maximum working pressure of 10,000 kg./sq.cm., but, in practice, pressures in excess of 7,000 kg./sq.cm. are seldom required. These machines have been in daily use for several years and have

given complete satisfaction. Instead of the usual type of expander, a form of conical ebonite roller is used. On certain types of padding mangles, the position of this roller, or even the conventional expander, was found to be a very important factor. These padding mangles have their bowls fitted in a triangular fashion. The two bottom bowls, of hard rubber, are fitted parallel to each other and set some distance apart. The top, soft rubber bowl rides on the two bottom bowls and supplies the pressure. With this type of padding mangle, a well of padding liquor builds up at the nip. It was found that, unless the roller was fitted so as to guide the cloth in a line bisecting the angle of the nip, the cloth would turn out slightly deeper in colour on one side or face.

Owing to the particular design of these machines, specky impregnation could occur if a non-foaming padding oil were not used. At one period, non-foaming padding oils could not be obtained. Trials were made with a variety of so called padding oils, all of which foamed to quite a high degree. The impregnating troughs with these machines are double; i.e. they have large- and small-capacity compartments fitted very close to the bottom rollers. When foaming of the padding liquor occurred, the foam spilled over into the larger compartment, where it was carried by the second roller into the already impregnated cloth, resulting in specky dyeings. The design of these machines and their impregnating tanks is such that visual inspection is practically impossible during operation. The use of these particular mangles has been discontinued for pigment padding.

The other two padding mangles are of the type having the pressure applied to the top bowl and have a maximum working pressure of 7,000 kg. per sq.cm.

In each padding mangle, the three bowls are equal in diameter (14 in.), and the hardness of the soft rubber bowls is 70° Shore. The wide mangles have bowls of somewhat greater diameter (16 in.), the soft bowls having the same hardness.

The impregnating troughs are of stainless steel provided with steam jackets, the height of the jackets being kept at 1 in. below the working level of the padding liquor. If the steam jackets are run to the top of the impregnating trough, there is always the danger of evaporation of some of the padding liquor that gets splashed on the portion of the tank above the working level, resulting in highly concentrated parts. These parts may enter the padding liquor, resulting in streaks or, if they get directly on the cloth, showing up as much darker spots. The tanks are rather narrower and deeper than is usual, with the immersion roller having as small a diameter as possible, but whipping or bending must be guarded against. The feed of the padding liquor is so arranged that it impinges on the sides of the trough. This arrangement gives better distribution of the fresh pad liquor and prevents dark places or lines, which would occur if the holes in the feed pipe were facing the cloth.

The temperature of the padding liquor in both the supply tank and the impregnating trough is kept the same. The actual temperature used depends on the weight of the cloth and also on the type of dye dispersed in the padding liquor. With the normal fine powder type of dye, it is 70°C. for pale and medium depths and 80°C. for heavy depths. With heavy qualities of linen, the top temperature is used for all depths. Dyes of the fine dispersed, powder fine, micro, and Colloisol types are padded at the lower temperature range of 60°C. for pale and medium depths and 65°C. for heavy depths. Again, the higher temperature (65°C.) is used for padding heavy qualities in all depths.

Working speed varies with the weight of the cloth and the weave, between 20 and 25 metres/min.

Expression (liquor take-up) has been standardised at 80% for the majority of the various qualities of cloth. The cloth is batched on rollers by means of a slipping clutch arrangement, which, unfortunately, is not entirely satisfactory on these padding mangles. The old system of batching direct against the top bowl is often criticised, yet the writer, after a very long period of dyehouse experience, has yet to have trouble from its use.

Until recently, it was necessary to use a padding oil to assist penetration by its wetting-out properties and, at the same time, to hold the dye particles in an excellent state of suspension over fairly long periods. Today, with the advent of the fine dispersed, etc. types of vat dyes, addition of a padding oil should be made with caution. Its use can, in some cases, cause aggregation of the minute dye particles, because of its incompatibility with the dispersant used by the dye manufacturer. Application of these particular dyes without addition of a padding oil has not, in the writer's experience, brought about any lowering of penetration of the dye.

After padding, the cloth is sent direct to the jigs without drying, as it has been found that the gain in intensity of colour does not compensate for the cost of slow drying. At the same time, the risk of boiling or sizzling, causing a spotted ("drying through") effect with resultant two-sided appearance, is avoided. This two-sided effect has occurred with padded cloth dried in an enclosed stenter owing to the hot air supply to one side being reduced by reason of a mechanical defect.

Care is necessary during running on to the jig to avoid creases or rub-marks, and any roller over which the padded cloth may have to pass should be free running. The strength of the padding liquor used is calculated so that a given percentage of it left over from the padding mangle is added to the reduction bath. This has been found preferable to making additions after a few ends in the reduction bath. Reduction and dyeing, shading, if necessary, follow the normal procedure. Oxidation varies according to the vat dyes used; incidentally, sodium chlorite seems to have certain advantages for this purpose, but its cost is rather high for bulk work.

Soaping-off is carried out in fully enclosed stainless-steel winces because of the ease of obtaining an efficient boiling treatment.

The writer is aware that some of the methods outlined above may be criticised by other experienced users of vat dyes. Nevertheless, the description given represents a system of pad–jig dyeing that has given least trouble in a dyehouse with a yearly production of more than 2,000,000 metres of dress and shirting linen cloth made from yarn varying from 16s lea to 50s lea.

In conclusion, the writer wishes to convey to Mr. Ellis Clayton his grateful appreciation of all the constructive criticism, advice, and suggestions received over many years in the field of the dyer's art.

LEANDRO N. ALEM 242
SAN ANDRÉS F.C.N.G.B.M.
ARGENTINA

(Received 9th July 1957)

Reference

[1] Nodder, *J. Textile Inst.*, **22**, 416 (1931).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

The Effect of Solvents in Dyeing

In a previous letter[1] we reported that, if a dyebath for the dyeing of cellulosic fibres with water-soluble direct dyes consists of a relatively large amount of a sparingly water-soluble solvent, e.g. *n*-butyl alcohol, and a small amount of water, the rate of uptake of dye is extremely rapid. In any given instance, maximum rate of uptake consistent with good levelness and penetration depends upon the presence of an optimal amount of water. If this amount of water is decreased, dye uptake becomes uneven and restricted to the surface of the material; if it is increased, the rate of dye uptake diminishes, and some dye remains in the excess water out of contact with the fibre.

Further work showed that a wide range of direct dyes and solubilised sulphur dyes of the Thionol M (ICI) type and also selected solubilised vat dyes behave in a similar manner in such solvent–water systems.

The greater the solubility of the dye in water, the more likely is it to pass from the hydrophobic solvent phase into the water phase associated with the cellulosic fibre. Consequently, simple acid dyes such as Kiton Fast Red G (C.I. Acid Red 1) are rapidly transferred from the external dyebath to the fibre surface, but, having little or no affinity for such fibres, they are readily removed when the material is subsequently washed in water.

Many of the recently introduced reactive dyes, e.g. Procion Brilliant Red 2B (ICI), are also quite water-soluble and should behave in the same way as conventional acid dyes. However, since they can combine irreversibly with the fibre, forming covalent linkages to its molecular structure, it seemed possible that satisfactory dyeings could be obtained with this type of dye, using such solvent–water dyebaths. When reactive dyes are applied by batch methods, e.g. on the jig or winch, dye absorption is relatively slow, and the degree of exhaustion obtained is very sensitive to the liquor ratio, the shortest possible liquors being desirable to obtain good exhaustion. The use of these solvent–water dyebaths reduces the effective liquor ratio very considerably, and should give a better tinctorial value, provided that it is possible to complete the dyeing operation by forming the covalent linkages between dye and fibre.

A sample of bleached, mercerised cotton cloth (2 g.) was immersed in *n*-butyl alcohol (100 c.c.) to which had been added a concentrated solution of Procion Brilliant Red 2BS (0·04 g.), previously dissolved in water (16 c.c.), at room temperature. The material was agitated vigorously in the dyebath, and the dye was rapidly transferred to the cotton, exhaustion being almost complete in 5 min. After 15 min. solid anhydrous sodium carbonate (0·1 g.) was added, and agitation continued for a further 15 min. The dyed material was then washed in cold water, and treated in a solution containing 2 g. Lensex 475 (Shell) per litre at 100°C. for 15 min. Very little loose colour was removed, and the final dyeing appeared to be perfectly uniform and well penetrated, while the tinctorial value obtained was very good.

The very low effective liquor ratio possible with such a solvent–water dyebath promotes rapid and complete transfer of dye from the external phase to the fibre. Lack of affinity of dye for fibre in the initial stages of the dyeing promotes penetration and levelling before final fixation.

Further experiments have shown that many solvents may be used to form the bulk of the dyebath. The possibility of using cheap solvents such as white spirit and trichloroethylene is particularly interesting. The solubility of water in such solvents is low, but it is possible to increase the water content of the system by incorporating suitable emulsifying agents. The experiment described above was repeated. The *n*-butyl alcohol was replaced by white spirit (100 c.c.), and the Procion Brilliant Red 2B was dissolved in a smaller amount of water (5 c.c.). The dyeing obtained was as deep as that obtained using a butyl alcohol–water dyebath although not quite so uniform. A small amount of water containing a little dye remained unabsorbed at the end of the dyeing.

We wish to express our thanks to Mr. W. E. Averill for his assistance in carrying out much of the experimental work referred to in this letter.

L. PETERS
C. B. STEVENS

DEPARTMENT OF TEXTILE INDUSTRIES
DEPARTMENT OF COLOUR CHEMISTRY AND DYEING
THE UNIVERSITY
LEEDS 2

28th January 1958

[1] J.S.D.C., **73**, 23 (1957).

ERRATA

Recommended Definitions (J.S.D.C., **74**, 44 (Jan. 1958))—

The definition of **skitteriness** † should read—

An undesired speckled effect in a yarn or a fabric arising from differences in colour or in depth of dyeing between adjacent fibres or portions of the same **fibre**.

Determination of Hydrogen Peroxide in Bleach Baths. AATCC Committee on Bleaching (J.S.D.C., **74**, 112 (Feb. 1958))—The first sentence should read—

Procedure—to approx. 20 ml. of distilled water add 10 ml. of the bleach bath and 20 ml. of dil. H_2SO_4.

Notes

Meetings of Council and Committees February

Council— 5th

Publications Committee— 18th

Fastness Tests Co-ordinating— 18th

Terms and Definitions— 6th

Review of Textile Progress— 21st

International Federation 1959 Congress—

Scientific and Technical Committee— 7th

Social Subcommittee— 12th.

Death

We regret to report the loss by death of Mr. T. M. Young.

A.S.D.C. Examination 1958

The annual examination for the Associateship of the Society of Dyers and Colourists will be held on Thursday, Friday, and Saturday, 29th, 30th, and 31st May 1958. Application forms are obtainable from the offices of the Society and must be completed and returned not later than 31st March 1958. Candidates should note that Papers A and B may be taken together, followed by C, D, and E; or papers A, B, and C may be taken together, followed by D and E.

Association Internationale de la Teinture Textile

The A.I.T.T. held its sixth congress at Enschede and Hengelo in the Netherlands on 13th and 14th June 1957 (*Teinture et Apprêts*, (41), 120 (June 1957)). The congress included meetings of the Association's three commissions— economic, technical, and prices. The first-named studied problems arising from the European Common Market and the possible formation of a Free Trade Area, and a working party was to be set up to make a more detailed study.

The Technical Commission was concerned with the standardisation of fastness testing in different countries (the A.I.T.T. has been recognised by the International Standards Organisation), abrasion resistance, and the effect of fluorescent brightening agents on colour fastness. While recognising the practical difficulties, the Commission expressed the wish that textiles should have labels indicating their suitability for washing and dry cleaning. The Commission studied methods of testing the waterproofing of fabrics, and approved the draft method of Professor Robinet (Belgium) for the determination of the shrinkage of wool fabrics, expressing the hope that the standards organisations of the different countries would adopt this method.

M. Pierre Baumgartner was re-elected president of the A.I.T.T. for the current year, during which the headquarters of the Association are to remain in Paris.

Textile Education in Switzerland

The Swiss textile industry (including the clothing and laundry industries) employs about 100,000 persons, of whom some 10,000 are concerned with textile finishing. Although, according to Dr. E. Brunnschweiler (*SVF Fachorgan*, **12**, 546 (Aug. 1957)), provision for education in textile technology appears to be adequate, conditions are far from satisfactory in the case of textile chemistry. Courses for dyers and textile chemists are available at the *Textilfachschule* in St. Gallen and the *Technikum* of the Canton Zürich at Winterthur. There is no *Hochschule* course in textile chemistry in Switzerland, though lectures on the subject are given in the University of Basle. There has been a serious decline in the numbers of students at St. Gallen and Winterthur and in the number of apprentices, but part-time refresher courses at the latter college have been well supported.

Floxan Cellulosic Fibre

According to the *SVF Fachorgan* (**12**, 592 (Aug. 1957)) the Spinnfaser AG., of Kassel, Germany, has placed on the market a special fibre, prepared by a modified viscose process. Floxan has a wool-like surface structure and a specially permanent crimp. It may be spun-dyed, or the usual dye classes for cotton and rayon staple may be applied. The new fibre is suitable for use in carpets, furnishings, car fabrics, blankets, and, blended with wool, in knitwear.

Foam Textiles

An article in *Textil-Rundschau* (**12**, 640–641 (Nov. 1957)) states that the first textiles made from foams (*Schaumstoff-Textilien*) have already appeared on the German market. The main characteristics of the Moltopren "foam fibre" are very low density, great bulk, and high thermal insulating power. Mixed with other fibres it is finding use especially in blankets, knitwear, and linings for winter coats, and interesting effects can be obtained in cloths for women's coats and costumes.

Yarns and fabrics containing "foam fibres" can be dyed and printed without further treatment. Attempts at mass coloration of the raw material during manufacture yielded results which are not fast to light, and the colour range is very limited. However, a process has now been worked out for dyeing the foam fibre in all colours desired.

New Books and Publications

Färberei

By E. Ulbricht. Pp. xiii + 242. Leipzig: Fachbuchverlag. 1957. Price, DM 16.80.

The aim of the author in preparing this work has been to provide both a broad introduction to textile chemistry for students and a modern review for specialists. He has been very largely successful in producing a work which should satisfy both. Understandably, the keynote has been condensation, but this spirit appears to have affected the choice of title. The book actually concerns itself, in the main, with the preparation and dyeing of cotton, with much shorter treatments of wool and silk and occasional references to viscose rayon. Compactness has been achieved by excluding illustrations and most of the theory, and with a commendable economy of words.

Water and water treatments are dealt with at the start, and few will question this pride of place. Then, because speciality chemicals figure largely in subsequent dyeing seccions, the second chapter is devoted to a survey of such compounds. The main portion of the work follows— the preparation and dyeing of cotton including the dyes used on cellulose; this section is very thoroughly covered. The book continues with the dyeing of wool and silk, and finally the author contrives to allot a little space to stripping, pH, degree of polymerisation, German fastness standards, and tables of recommended dye fastnesses for various purposes.

There is much to admire in this effort. Although it is modest in size, the coverage is thorough and systematic. Readers whose introduction to colour chemistry was free from B.I.O.S. will immediately feel at home with the old familiar dye names, and those who complain of the hedging of technologists will rejoice in the complete absence of *vielleicht* and *wahrscheinlich* from this work. On the other hand, the breadth of the page makes the print difficult to scan, and this state of affairs is not helped by the absence of illustrations, which. if they perform no other function, prevent fatigue. For a book carrying such a broad title, the allocation of space is inclined to be a little unbalanced: the animal fibres are treated at the wrong liquor ratio, with equal weight being given to water as to wool. One feels that it should have been possible, by pruning, for example, the data on domestic water consumption and the hardness of various town supplies, to have found more room for wool and silk.

A very serious error indeed is the omission of all references to machinery, and this constitutes the main weakness of the book under its present title. In view of its strongly practical tone, it seems a pity not to have rounded off the book with notes on the mechanical side of dyeing.

Färberei is informative, easily read, laconic, and perhaps a little unquestioning. To students and teachers in part-time classes, and indeed all other hard-pressed people, it should have a strong appeal.

S. R. Cockett

Reports on the Progress of Applied Chemistry

Volume XLI 1956

London: Society of Chemical Industry. [1957.] Pp. 795. Price, 100s. 0d.

In its contents this new volume follows the pattern of the previous reports.

In the section on textiles and plastics W. A. Richardson reviews progress in the production of viscose rayon yarn, high-tenacity rayons, and crimped fibres, and Dr. J. F. Keggin surveys recent studies on protein fibres and refers to the considerable interest in the use of solvents for scouring raw wool. It is claimed that this type of scouring gives less fibre entanglement and hence improved performance during subsequent processing of the wool. Butyl alcohol, polyhydric or keto-alcohols, and other solvents are recommended for this purpose (*BP* 739,166 and 738,014; *USP* 2,717,901 and 2,723,281).

The chapter on synthetic fibres comprises sections on polyester fibres (written by Dr. R. J. D. Smith), and on further studies on methods for the manufacture of terephthalic acid; on acrylic fibres (J. F. Lloyd Roberts), wherein intensive activity has been fully sustained in Britain, Germany, and the U.S.A. O. B. Edgar reviews studies on polyamide fibres. The production of all synthetic fibres is steadily increasing, and it is estimated by the U.S. Material Policy Committee that 4 thousand million lb. of synthetic fibres will be produced annually by 1975, consisting of— acrylics 1·2, nylon 1·0, polyesters 0·8, and miscellaneous 1·0 thousand million lb.

In the section on textile finishing A. J. Hall mentions particularly improvements in dyeing natural and synthetic fibres, the advent of the Procion (ICI) dyes, so useful for producing fastness to washing, as they combine chemically with the fibres. He also refers to developments in finishing, to new studies on crease-resist finishing of cotton and regenerated cellulose fibre fabrics, to wash-fast and non-ironing fabrics, and to non-woven goods.

K. Burrow surveys progress in detergents, with Britain now the second largest user of synthetic detergents in the world, having a consumption of 200,000 tons in 1955, which represents 37% of all soaps and detergents used in Britain. Dodecylbenzene continues to be by far the most used raw material for detergents. There are also references to improvements in the technical properties of detergents, the effect of the addition of brightening agents to washing powders, and new methods for evaluating fabric detergency.

Under *Intermediates and Dyestuffs* Dr. H. E. Nursten reports that, although 1956 marked the celebration of the centenary of the production of synthetic dyes by William H. Perkin, pride in this achievement has been damped by the commercial results in 1955, the amounts of dyes exported during that year being less than in 1954. But one of the outstanding achievements in 1956 was the new class of reactive dyes, the Procions being described as relatively simple, containing a labile

chlorine atom which enables them to react under mildly alkaline conditions with fibres to give extremely good light and washing fastness.

Cationic surface-active agents have been very useful additions to basic constituents of road materials to improve performance and reduce road construction costs.

As before, there are comprehensive literature and patent references at the end of each chapter, and there is also a well compiled name and subject index. It is an indispensable and excellent guide and reference book. A. F. KERTESS

Resonance in Organic Chemistry

By G. W. Wheland. Pp. xiii + 846. New York: John Wiley & Sons Inc. (London: Chapman & Hall Ltd.). 1955. Price, 120s. 0d.

Resonance in Organic Chemistry is the title of a revised and expanded version of Professor Wheland's earlier work, *The Theory of Resonance and its Application to Organic Chemistry.*

The text is divided into nine chapters and an appendix (of 88 pages) containing the interatomic distances and bond angles of a considerable number of organic compounds. The first eight chapters consist of qualitative discussions of the nature of valency and of the resonance theory and its application in interpreting the effects which structure and configuration have on the distribution of electrons in the molecules of organic compounds as reflected by their physical (e.g. dipole moments, absorption spectra) and chemical (e.g. orientation of substituents in aromatic substitution, strengths of acids and bases) properties. Readers not versed in the theory of wave mechanics will benefit from the general clarity of the exposition in these chapters, although they may find parts rather heavy going because of the author's anxiety not to create misleading impressions. Chapter IX can be profitably read only by those with a knowledge of higher mathematics, since it is devoted to an account of the mathematical basis of the valence bond (resonance) and molecular orbital theories of chemical bonding. The appendix is a useful compilation of data and the indexing is good.

The book is well produced and bears the mark of careful proofreading. Because of its price, although this is not excessive when compared with the prices of books of similar size and content, it will probably be more frequently found on library bookshelves than on those of less affluent chemical practitioners.

N. H. P. SMITH

Farbnamenlexikon von A bis Z

By Georg Seufert. Pp. 305. Göttingen: Musterschmidt-Verlag. Price, DM 16.80.

For the reason, set out in the introduction, that patterns fade but words and numbers persist, descriptions of some 2000 dye and colour names have been compiled. There is a reasonable choice of methods for the characterisation of colour, but at which point in this range the author takes his stand is by no means clear. The task of describing colour in words alone is well nigh impossible, but the fact that he has at least shown willing tends to temper undue criticism. Where words are unavoidable, as in the case of the gestalt attributes of colours, the author has been more successful; in other cases the difficulties become insurmountable, and after referring the particular colour under discussion to a second, third, or fourth colour, a final appeal has to be made to Ostwald, the British Colour Council, or other authorities. Before the first milestone of A has been passed, the road is being paved by reference to a pattern, and this a Dutch postage stamp issued twenty years ago. Colour names and dye names are mixed indiscriminately, a number of the examples being obsolete. One must obviously approach with diffidence foreign words capable of such fine shades of meaning as the names of colours; but with dye nomenclature, one is on safer ground. It would have been better to have left out dyes entirely in view of the more comprehensive and up-to-date information already available in other works of reference; but perhaps the examples quoted are those of particular interest to artists rather than to dyers. In this case, however, it should not be necessary to include snippets of dye chemistry.

The essay with which the book concludes—*Colour in the Life of Woman*—turns out to be a discourse on the matching of colours in dress, with some philosophy on that type of beauty which has no connection with truth. Were it not for the loss that the humour of nations would sustain, this portion could safely be omitted in any further edition.

The dictionary will prove, no doubt, valuable in German-speaking countries to artists and the fashion world in general—or indeed anyone requiring a quick reference to a colour name without the necessity of reproducing the colour. To those concerned with accurate colour matching in the industries from which the Society draws the bulk of its members, its value is limited.

S. R. COCKETT

A History of the West of England Cloth Industry

By K. G. Ponting. Pp. 168. London: Macdonald & Co. (Publishers) Ltd. 1957. Price, 15s. 0d.

Wool cloth has been made in the West of England for 4,000 years, but an industry making the bulk of its products for sale dates only from the middle of the thirteenth century. It is these last 700 years of history that are dealt with in this book. The author has the great advantage of having been brought up in the trade, as were his ancestors for several generations back. His great-grandfather was one of the last hand-loom weavers, and the account of the dying struggles of that type of industry are based on his grandmother's account of the experiences of her youth. Thus Mr. Ponting is familiar with all the technical details of the trade in a manner that very few authors of such books have been.

The story he tells is most absorbing and pleasant to read, and it is interesting to note how problems that beset our ancestors still beset us. But the book is not merely pleasant and interesting reading about bygone days and practices: it also

holds lessons for us today, at a time when such great stress is being laid on the vital necessity for technological training. One of these lessons is that it is not enough to be in the forefront of technological advance. The West of England industry was technologically equal to that of any other district in the world: indeed, some of the more important machines used today in the woollen industry, e.g. the rotary milling machine, originated in that industry, and West of England cloths have never been surpassed by any others of their type. The decline of the West of England industry during the last 150 years was not caused by technological inferiority but, among other things, by the facts that either customers no longer wanted the type of cloths it made or, if they did, had not the money to pay for them. It would seem that one of the main reasons why supremacy in the wool cloth trade passed from the West of England to the West Riding of Yorkshire was that the industry in the latter region was much more flexible and ready to change the type of products it made— the Bradford trade has changed completely more than once in the last century— than was that in the West of England. It is because the reading of this book makes such facts apparent that it should be read by all in any way connected with the manufacture of textiles, or indeed the manufacture of anything.

C. O. CLARK

New Books received

Proceedings of the Work Study Conference for Senior Work Study Practitioners and Works Managers 1957. London: Association of British Chemical Manufacturers. 1957. Pp. v + 206. 13s. 6d.

Recueil des Formules et Tables de Colorimetrie à l'usage des laboratoires industriels. F. BRAUN. Brussels: Edition-Librairie-Publicite Internationales. 1956. Pp. 61. 250 Belgian francs.

Manuel d'Initiation à l'Etude de la Science des Couleurs. F. BRAUN. Brussels: Edition-Librairie-Publicite Internationales. Pp. 59 + 1 colour plate. 350 Belgian francs.

Test for Trash Content of Cotton and Waste by the Shirley Analyser. BS.2889. London: British Standards Institution. 1957. Pp. 8. 3s. 0d.

Cotton Belting Ducks. BS.1069. London: British Standards Institution. 1957. Pp. 9. 4s. 0d.

Cotton Fabrics for the Reinforcement of Rubber Hose. BS.1103. London: British Standards Institution. 1957. Pp. 8. 3s. 0d.

Description of Woven and Warp-knitted Fabrics containing Man-made Fibres. BS.2935. London: British Standards Institution. 1957. Pp. 6. 2s. 6d.

Tracer Applications for the Study of Organic Reactions. J. G. BURR JR. New York: Interscience Publishers Inc. 1957. Pp. x + 291. $7.50.

Supplement to "The Law of Copyright". Butterworths Annotated Legislation Service. Statutes Supplement No. 100A. J. P. EDDY assisted by E. ROYDHOUSE. London: Butterworth & Co. (Publishers) Ltd. 1957. Pp. v + A1–A46. 7s. 0d.

Historical Notes on the Wet-Processing Industry. S. M. EDELSTEIN. New York: Howes Publishing Co. Inc. Pp. 54.

Wasserdichtmachen in Rezeptform. R. GÜNTHER. Mönchen-Gladbach, Germany: Lapp-Verlag. 1957. Pp. 169. DM 5.85.

The Chemical Industry during the Nineteenth Century. A Study of the Economic Aspect of Applied Chemistry in Europe and North Africa. London: Clarendon Press: Oxford University Press. 1958. Pp. x + 292. 45s. 0d.

Methoden der Organischen Chemie. (Houben-Weyl). Band I. *Teil 1. Allgemeine Laboratoriumspraxis.* Edited by E. MÜLLER. Stuttgart: Georg Thieme Verlag. 4th edition 1958. Pp. xlii + 1048. DM 198.00.

Encyclopedia of Chemical Technology. First Supplement Volume. Edited by R. E. KIRK and D. F. OTHMER. New York and London: Interscience Publishers Inc. 1957. Pp. xviii + 974. $25.00.

Cereal Carbohydrates. I. A. PREECE. *Lectures, Monographs and Reports 1957. No. 2.* London: Royal Institute of Chemistry. Pp. ii + 24.

Der Wollstoff-Appreteur. K.-H. SCHICKTANZ. Heidenheim/Brenz, Germany: Verlag Alfred Halscheidt. Pp. 97. DM 7.80.

Reports on the Progress of Applied Chemistry. Volume XLI–1956. Edited by H. S. ROOKE. London: Society of Chemical Industry. 1957. Pp. 795. 100s. 0d.

Disposal of Industrial Waste Materials. London: Society of Chemical Industry. 1957. Pp. iv + 157.

Fibre Microscopy. Its Technique and Application. J. L. STOVES. London: National Trade Press Ltd. 1st edition 1957. Pp. viii + 286. 50s. 0d.

The Dissemination of the Knowledge of Soviet Scientific Work in Western Countries. A. E. STUBBS (*Reprint from Aslib Proceedings, Volume 9, No. 11*). London: Aslib. 1957. Pp. 8.

Costing in the Textile Bleaching, Dyeing and Printing Trade. TEXTILE FINISHING TRADES ASSOCIATION. London: Sir Isaac Pitman & Sons Ltd. 1st edition 1957. Pp. x + 67. 21s. 0d.

Review of Textile Progress. Volume 8. 1956. Manchester and Bradford: Textile Institute and Society of Dyers and Colourists. 1957. Pp. 611. 42s. 0d. or $6.00.

Färberei. E. ULBRICHT. Leipzig: Fachbuchverlag. 1957. Pp. xii + 242. DM 16.80.

The Book of pH. R. B. WEBBER. London: George Newnes Ltd. 1st edition 1957. Pp. 111. 30s. 0d.

Proceedings of the Perkin Centennial 1856–1956. Edited by H. J. WHITE, JR. Lowell, Massachusetts: AATCC. 1957. Pp. x + ix + 467. $10.00.

The Measurement of Colour. W. D. WRIGHT. London: Hilger & Watts Ltd. 2nd edition 1958. Pp. x + 263 + 8 plates. 52s. 0d.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

New Aspects of the Pad-Roll System

B. Mellbin

Amer. Dyestuff Rep., **46**, 770–776 (21 Oct. 1957)

When the Pad–Roll system is used in dyeing, the cloth is rolled after padding under carefully controlled conditions of temperature and humidity. A long time at elevated temperatures is allowed for the dye to diffuse into the fibres, and thus even dyeing is ensured. The system can be used in desizing, where the careful control which is possible again ensures evenness in subsequent dyeing operations. Cotton can be boiled-off under the same careful control using the Pad–Roll machine. It is shown

that sodium chlorite acts as a bleaching agent most efficiently when the liquor ratio is high—conditions for the best utilisation of sodium chlorite in a Pad–Roll machine are given (pH 6·5–7·0; 90°c.). P.T.S.

Application of Fluid Beds to Textile Processing
F. G. Audas, C. G. Badcock, W. McNabb, and J. A. Wilson
J. Textile Inst., **48**, P 767–P 776 (Dec. 1957)

Air is passed upwards through a bed of particles 0·1–1·0 mm. in diameter, and the movement of the particles (sand or glass) is controlled by the pressure of the air stream. Fluid beds remove or supply heat very rapidly, and have many potential uses in textile processing. The engineering problems which still remain should not be insuperable.

Experiments show that fluid beds can be used to dry fabrics, to bake resin finishes, to fix disperse dyes on Terylene, nylon, and cellulose triacetate and secondary acetate, and to apply azoic dyes to Terylene, nylon, and triacetate. Blends of cellulosic and hydrophobic fibres can be dyed with disperse, azoic, or reactive dyes using a fluid bed. Nylon can be singed by passing it rapidly through a fluid bed above its melting point—the outer fibres approach the temperature of the bed. Improved dyeability is said to result. P.T.S.

PATENTS

Carbon Black Furnaces
Phillips Petroleum Co. *BP* 786,089

Wet Treatment of Yarn on Yarn Advancing Rollers
Celanese Corpn. of America *BP* 785,146

The yarn passes over a series of yarn advancing rolls on one or some of which it is treated with a liquid. A wiper has a resilient upper surface which engages one of the rolls and a lower surface engaging another of the rolls so that liquid wiped off the first roll is transferred to the next roll. C.O.C.

Sizing Machines with One-way Air Driers
Maschinenfabrik Ruti *BP* 788,558

Beam on which Fabric is Wound to be Wet Processed
Celanese Corpn. of America *BP* 785,093

A beam on which fabric is wound to be dyed or otherwise wet processed has radially-extending members bearing pins or the like to engage the selvedges of the rolled fabric and so prevent it from shrinking or shifting. C.O.C.

Jig
A. Libbrecht and P. Libbrecht *BP* 787,822

A jig has a rocker device for spreading the fabric, the device having fabric deflecting rollers. This device rocks toward the receiving roll in response to reversal of the direction of travel of the fabric. Adjustable abutment means co-operate with the rocker device to prevent it rocking to within a predetermined distance from the receiving roll. C.O.C.

Obtaining Dyed Samples of Cloth from Pressure Dyeing Machines
F. Smith & Co. (Whitworth) *BP* 787,081

Tensioning Rollers for Stretching Fabric Weftways
H. Bechter *BP* 787,995

Applying Liquid to Cloth, Paper, Film, etc.
Hall Harding *BP* 788,939

A driven roller applies the liquid directly to the cloth. The liquid is fed to this roller by a second driven roller to which the liquid is directly applied. These two rollers have parallel axes and are so close to one another that the liquid is attracted capillary from the one to the other roller when they are rotating. The first roller is driven independently of the material to be treated and both rollers are driven in the same rotary direction so that their adjacent surfaces have opposite angular movement. C.O.C.

Calenders
Hunt & Moscrop *BP* 788,450

The bottom bowl is supported on one or more lines of rollers, each roller being mounted in independent bearings which are adjustable at right angles to the vertical plane through the longitudinal axis of the bowl. This prevents bending of the bowl. C.O.C.

Spreading Tricot Warpknit Fabric
American Viscose Corp. *USP* 2,747,250

A treating tank through which the fabric is conducted to flatten its selvedges. An elongated nozzle mounted above the tank has several orifices which discharge liquor outwardly against the selvedges as the fabric approaches the bath and keeps them flattened against an inclined backing plate. The nozzles can be adjusted to deal with different types of fabric and fabrics of different widths. C.O.C.

Controlling the Lateral Position of Cloth, Paper, etc. while in motion
Siemens-Schuckertwerke *BP* 786,120

Tenter
Famatex *BP* 785,929

An arrangement which enables the filters for the drying medium to be readily and quickly cleaned. C.O.C.

Pin Bars for Tenters working at High Temperatures
Famatex *BP* 785,484

Cylinder Drier
Samcoe Holding Corpn. *USP* 2,750,679

A machine in which the cloth is dried and allowed to shrink to the maximum extent. C.O.C.

Drying Tubular Fabric
Fitch Textile Co. *BP* 789,648
USP 2,750,649

Air or Gas Distribution under Fluidised Beds
Huntington Herberlein & Co. *BP* 786,749

Automatic Control of the Printing Paste Feed in Screen Printing
Gebr. Stork & Co.'s Apparatenfabriek *BP* 787,948

Apparatus for the screen printing of cloth uses several stencil frames, the feed of printing paste to each frame being automatically controlled. C.O.C.

Cleansing Textile Print Wash Blankets
W. R. Grace & Co. *USP* 2,747,506

An arrangement for carrying out the process described in *USP* 2,723,932. C.O.C.

Drying Paper or Cloth
Schnellpressenfabrik Frankenthal Albert & Cie.
BP 788,254

Drum drier expressly designed for use in conjunction with photogravure printing. C.O.C.

Conditioning Cloth, Paper, or the like in a Closed Chamber
Aktiebolaget Svenska Flaktfabriken *BP* 785,243

The material is passed through a conditioning chamber divided into sections, the material being cooled between each section to a temperature below that of the section it has just left. The RH progressively increases from section to section. By this means rapid conditioning is obtained. C.O.C.

Driving Mechanism for Raising Machines
J. F. Casajoana *BP* 785,512

Means which enable stepless variation in the speed of the raising cylinders thus increasing the rate of production and control of the degree of raising. It also gives very smooth variation in the speed of the rollers and prevents vibration whichever speed the machine may be run at. C.O.C.

Raising Machines
Tomlinson's (Rochdale) *BP* 787,028

A machine which gives clear indication when the cylinders are being driven at the appropriate speeds to give zero raising action. C.O.C.

Spring Padding Units for Textile and Garment Finishing Machinery
D. & J. Tullis *BP* 786,066

Automatic Application of Transfers to Garments
J. E. Kienel *BP* 785,769

Apparatus for Coating Paper with Mineral Pigments
Kimberly-Clark Corpn. *USP* 2,749,878

Apparatus in which the rolls are arranged so that the force applied to the rolls in the auxiliary train and the pressure at the coating nip can be readily adjusted within very closely defined limits. C.O.C.

Drying Machines for Coated Textiles, Paper, etc.
W. Adshead *BP* 787,281

Drying or removal of surface water from coated or impregnated webs is improved by directing jets of compressed air, which may be heated, against opposite sides of the web. The drying equipment permits greater operating

speeds and is specially advantageous for low melting point coatings and plastics applied to webs of paper, textiles, etc. G.S.B.

Continuous Drum Drying Machine for use in Laundries
F. Plümer *BP* 787,942

Treating Permeable Sheets with Fluids
Secotan *USP* 2,749,737

Modification of *USP* 2,702,229 (J.S.D.C., **72**, 109 (1956)). Positioning the sheet in the apparatus and forcing the membrane against the bed are simplified. This together with increasing the pressure of liquid necessary to separate the membrane from the edges of the sheet enable the liquor to be delivered to the sheet at a higher pressure and higher rate. C.O.C.

New Products developed since November 1956— Alphabetical List (IV p. 192)

Compressive Shrinking (X p. 213)

Flexible Coated Sheeting (X p. 213)

II— WATER AND EFFLUENTS

Colour Removal from Azo Dye Wastes
N. L. Nemerow and W. L. Wilson
Ind. Eng. Chem., **49**, 77 A–78 A (Dec. 1957)

Stannous chloride is an effective reducing agent for decolorising effluents containing azo dyes. Examples are given of the quantities required to decolorise typical mono-, dis-, and tris-azo direct dyes in dilute solution, and the economics of the treatment are considered. W.K.R.

Wool Industry Effluent
J. Nowacki
Gaz, Woda i Technika Sanitarna, (3), 65–90 (1956): *Polish Tech. Abs.*, (25), 69 (1957)

Effluent containing acid chrome and metachrome dyes is purified with sulphuric acid and ferrous sulphate, and mixed in the equalisation tank with effluent from washhouses and from dyeing departments using sulphur dyes, previously purified by coagulation with milk of lime and ferrous sulphate. Subsequently, passing the effluent through a sedimentation tank represents the final stage of the local purification process. C.J.W.H.

Purifying Effluent from the Natural Silk Industry
A. Chojnacki and J. Zabowski
Gaz, Woda i Technika Sanitarna, (1), 16–21 (1956): *Polish Tech. Abs.*, (25), 83 (1957)

Attempts were made to purify sewage from a plant manufacturing natural silk. The plant produced sewage at a rate of 73 cubic metres per 24 hr. Good results were obtained by preliminary purification of sewage by coagulation with iron salts and liming. Coagulation of sewage with chlorinated ferrous sulphate and liming proved highly satisfactory. In the course of the purifying process, lime should be introduced first, and then the chlorinated ferrous sulphate. Depending on the concentration of the sewage, the minimum–optimum doses were found to be (in mg./litre)— CaO 424–360, $FeSO_4.7H_2O$ 850–720, chlorine 106–128. A flocculent mass of medium dimensions settles in the Imhoff funnel after as little as 1 hr. The sediment dries badly and is difficult to dehydrate. C.J.W.H.

PATENTS

Lime Soda Water Softening Plant
Aquamatic *USP* 2,749,304

Apparatus having improved means for adding the reagents, removing the sludge and controlling the working cycles. C.O.C.

Preventing Corrosion of Metal Pipes by Water Softened with Phosphates
Gebruder Giulini *BP* 785,626

Addition of 0·5–10·0% of crystalline silicic acid on the weight of phosphate used stops the treated water from corroding metal pipes. C.O.C.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Turbidity and Viscosity Measurements on Some Cationic Detergents in Water and in Sodium Chloride Solutions
L. M. Kushner, W. D. Hubbard, and R. A. Parker
Bur. Stand. J. Res., **59**, 113–119 (Aug. 1957): *Research Paper* 2778

Light-scattering and viscosity measurements were made on solutions of dodecylamine hydrochloride, dodecyltrimethylammonium chloride, and tetradecyltrimethylammonium chloride in water and in sodium chloride solutions. From the data, the micellar weight and intrinsic viscosity of the micelles of each detergent were calculated. The effect of the concentration of sodium chloride on these values is discussed. W.K.R.

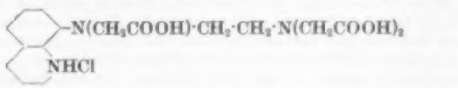
Fibre to Fabric with Glycerol— I
E. A. Parolla and C. Z. Draves
Amer. Dyestuff Rep., **46**, 761–769 (21 Oct. 1957)

A survey of the uses of glycerol in the textile industry, which include lubrication, sizing and softening. Glycerol is used as a plasticiser in resin finishes. Its hygroscopicity makes it a useful component of antistatic finishes. Details of its use in other finishes are given. The most important use of glycerol is in the manufacture of alkyd resins. Important derivatives of glycerol are the dichlorohydrins, which are used to etherify cellulose, epichlorohydrin, which is a dye intermediate, and the monoglycerides of fatty acids, which are used as emulsion stabilisers. 73 references. P.T.S.

PATENTS

Quinolyl and Pyridyl Aliphatic Alkylene Polyamine Polyacid— Chelating Agents
Dow Chemical Co. *USP* 2,751,386

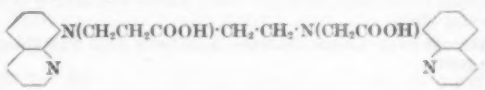
When one of the amino H atoms of an aliphatic alkylene polyamine is replaced by a quinolyl group and the other amino H atoms are replaced by acetic acid or higher fatty acid groups, the quinolyl polyamine polyacetic acid and its alkali metal, NH_4 or amine salts form water-soluble chelates with a larger number of mono- and polyvalent metals than do the alkylene polyamino polyacetic acid compounds in which all the amino H atoms have been replaced by acetic acid. An example of such a compound is



obtained by replacing 8-bromoquinoline with ethylenediamine for 5 hr. and condensing the product with NaCN and HCHO.

USP 2,751,387

Replacement of two of the amino H atoms by quinolyl groups yields products which are extremely powerful chelating agents for the heavy metals. Thus Cu is very strongly complexed by



USP 2,751,389

Replacing the quinonyl group of the compounds described in *USP* 2,751,387 (above) by a pyridyl group yields excellent chelating agents for the alkaline earth and rare earth metals and for Pb, V, Zr and U.

USP 2,751,391

Replacing the quinonyl group of the compounds described in *USP* 2,751,388 (above) by pyridyl groups yields products which yield very stable chelates with heavy metals of the transition group. C.O.C.

Increasing the Viscosity of Aqueous Solutions of Surface-active Compounds
W. A. Scholten's Chemische Fabrieken NV *BP* 786,252

Addition of a small amount of a water-soluble simple or mixed alkyl ethers of cacos bean gum, preferably Me hydroxyalkyl ethers, considerably increases the viscosity of both dilute and concentrated aqueous solutions of surface-active compounds. C.O.C.

Water-in-Oil Emulsions
N.V. de Bataafsche Petroleum *BP* 786,596

The stability of water-in-oil emulsions obtained by using a polyvalent metal salt of an organic sulphonic acid as the emulsifier is much improved if the emulsifier is used together with an alkyl phenol. C.O.C.

Solvents, Swelling Agents and Softeners for Polyester Fibres, Films, etc.
FH *BP* 786,886

Primary, secondary, and tertiary aromatic amines or heterocyclic amines containing N in the nucleus and an exocyclic group are good solvents, swelling agents and softeners for polyesters or terephthalic acid with aliphatic dihydroxy compounds. Among the amines listed as being suitable for these purposes are aniline, a 1:1 mixture of 1- or 2-naphthylamine and benzylalcohol, and 5:6:7:8-tetrahydro-2-naphthylamine. C.O.C.

Solvent for Acrylonitrile Polymers
Chemstrand *BP* 787,060

Mixtures of ethylene sulphite and *NN*-dimethylacetamide, *NN*-dimethylformamide or moist nitromethane are excellent solvents for polymers containing $\leqslant$ 70% of acrylonitrile. The solutions are lighter coloured than those produced by hitherto known solvents. C.O.C.

Solvents for Polyalkylene Terephthalates
Gevaert *BP* 788,363

Chloralhydrate gives clear and stable solutions of polyalkylene terephthalates at comparatively low temperatures, e.g. 65°C. The solutions are colourless, they may solidify at lower temperatures, but readily reform the clear solution on being warmed. C.O.C.

Antistatic Agent for Hydrophobic Staple Fibres
FH *BP* 786,953

Processing of hydrophobic staple fibres, e.g. Perlon, is improved by impregnating with a salt of a low-molecular vinyl or alkyl polymer containing sulpho groups which are bound to the rest of the polymer through C, O or S, e.g. polystyrene sulphonic acid. W.G.C.

Antistatic Finish for Synthetic Fibres
ICI *BP* 788,079

A polymeric quaternary ammonium compound produced from a monomer of formula

$$CH_2{:}C(R^1)\cdot CO\cdot NH\cdot R^2\cdot N(\textit{tert.})X$$

(R^1 = H or CH_3; R^2 = alkylene radical whose C chain may be interrupted by hetero atoms; N(*tert.*) = aliphatic or heterocyclic tertiary amine; X = monovalent anion) e.g. N-(β-diethylaminoethyl)-methacrylamide, are used as antistatic agents for synthetic fibres. The antistatic finish obtained is unaffected by subsequent normal processing or by washing with soap and soda. C.O.C.

Silicon-containing Antistatic Compositions
Mitsubishi Rayon Co. *BP* 787,941

The colloidal solution obtained by treating an alkyl acetate, a monohydric aliphatic alcohol, and a silicon halide with water is an excellent antistatic agent, e.g. the product obtained by stirring together ethyl acetate (500), silicon tetrahalide (40), and ethyl alcohol containing 10% water (550). C.O.C.

Nitrogenous Condensates— Auxiliary and Finishing Agents
Ciba *BP* 787,733

Alkylene polyamine of 2–6 N containing a non-aromatic hydrocarbon of > 7 C directly linked to N and one or more hydroxyalkyl groups of > 1 C also linked to N, or mono-N-acylation derivatives are condensed with a N-methylolamide of an aliphatic or *cyclo*aliphatic carboxylic acid of > 7 C or a N-methylolmethane of an aliphatic or *cyclo*aliphatic alcohol. The products or their salts or quaternary ammonium compounds have wide uses as softening agents, resin finishes, etc. C.O.C.

N-Vinyloxyalkylalkanecarboxamides
Rohm & Haas *BP* 786,927

Compounds of formula $CH_2{:}CHOANR^1COR^2$ (A = C_2–C_3 alkylene group having at least 2 C atoms in a chain separating the adjoining ether O and N atoms; R^1 = H or CH_3; R^2 = Alk of 11–17 C), e.g. the product obtained by treating an aminoalkylvinyl ether with methyl or ethyl laurate or stearate, can be readily formed into mono- or co-polymers. Such polymers have a wide use as auxiliary agents in many industries. C.O.C.

Vinyl Ethers of Substituted Biurets
Rohm & Haas *BP* 787,045

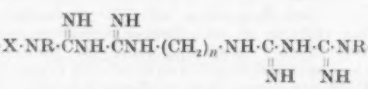
Compounds of formula $CH_2{:}CHOANRCONHCONH_2$ (A = divalent, saturated aliphatic or *cyclo*aliphatic group of 2–18 C of which at least 2 separate the O and N atoms adjacent to A; R = H, aralkyl, Alk of 1–18 C or *cyclo*alkyl), e.g. the product obtained by treating $CH_2{:}CHOCH_2{\cdot}CH_2NH_2$ with methyl allophenate, are readily formed into homo- or co-polymers. Both monomers and polymers have a very wide range of uses as resinous materials both in forming fibres, modifying other polymers, as textile finishes, ingredients for paints, improving the wet strength of paper, etc. C.O.C.

Werner-type Chromium. III— Compounds containing Inorganic Acid and Carboxylic Acid Radicals
Svenska Oljeslagerі *BP* 788,539

A carboxylic acid, a neutral salt of trivalent chromium with a strong monobasic mineral acid and a salt of a strong inorganic base with a weak acid are heated together in an anhydrous organic solvent soluble in or miscible with water. The inorganic precipitate is separated off and the Werner-type compound isolated or used directly in the form of the solution obtained. The products have wide uses, e.g. in the treatment of textiles or leather. C.O.C.

Biguanides— Rot and Mothproofing Agents
ICI *BP* 785,937

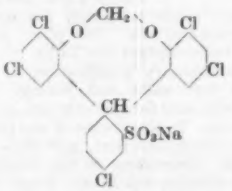
Compounds of formula—



(A = phenyl which may be substituted by Alk, alkoxy, NO_2 or Hal; X = alkylene of > 4 C; R = H, Alk or aralkyl; *n* = 2–12; the polyethylene chain may be interrupted by O atoms and/or aromatic nuclei), e.g. 1:6-di-(N_1 : $N_1{}^1$ - benzyldiguanido - N_5 : $N_5{}^1$) - hexane tetrahydrochloride, are rotproofing agents for use with wood pulp and rubber latex. They are also used for controlling slime in paper mills and as mothproofing agents for textiles. C.O.C.

Mothproofing Agent
FBy *BP* 785,080

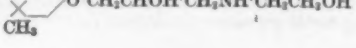
Methylene ethers of sulphonated *oo'*-dihydroxytriphenylmethane are excellent mothproofing agents. Mixed with 25% of their weight of dibutyl ethers of salts of 2:2'-dihydroxytetra(or penta)chlorotriphenylmethane sulphonic acids they yield aqueous solutions which do not foam and are stable for long periods. Thus 1·5–2·5% by weight of a mixture of 3 parts of



and one part of Na 2:2'-di-*n*-butoxy-3:5:3':5'-4''-pentachlorotriphenylmethane sulphonate, boiled with 20 times its weight of water and added to an acid dyebath at 35–40°C., dyeing then being conducted as usual, imparts a mothproof finish fast to subsequent manufacturing processes, wear and light. Such a mixture can also be applied from a peroxide or hydrosulphite bleaching bath. C.O.C.

Dyeing and Printing Cellulose Acetate, Nylon, Polyester Fibres or Films, and Cyanoethylated Cellulose
S *BP* 785,486

Compounds of formula $R_m{}^1\cdot A(OR^2)_p$ (A = an aromatic hydrocarbon radical which may be halogenated; R^1 and R^2 = H, Alk or aminoalkyl; *m* and *p* = 1 or 2; either R^1 or R^2 must be aminoalkyl) e.g.



increase the affinity of the above substances for acid and disperse dyes. They may be incorporated in these substances before they are extruded, or the materials may be impregnated with them, or they may be added to the dyebath or the dyeings may be aftertreated with these compounds to give increased fastness to gas fume fading. C.O.C.

Monoazo Compounds as Absorbents for Ultraviolet Radiation
ICI *BP* 786,907

Compounds of formula $A^1N{:}NCHXY$ (A^1 = benzene substituted by at least one SO_2H group and, if desired, also by Cl, Br, CN, CF_3, COC_6H_5, COOH, SO_2Alkyl, COOAlkyl or $CONR^1R^2$ (R^1 and R^2 = H, Alk, *cyclo*Alk, Ar or aralkyl); X and Y = $COCH_3$ or $CONH_2$), e.g. 2-chloro-*p*-toluidine-5-sulphonic acid diazotised and coupled with malodiamine or acetyl acetone, are useful for adding to paints, plastics, regenerated cellulose sheeting, etc., to prevent either them or articles to which they are applied or in which they are wrapped from being affected by ultraviolet radiation.

BP 786,908

Compounds of formula $A^1N{:}N{\cdot}CHYCN$ (Y = CN, COH_2 or $CONH_2$), are similarly used.

BP 786,909

Compounds of formula $A^2N{:}NCHXY$ (A^2 = benzene substituted by at least one $SO_2NR^1R^2$ group and, if desired, also by Cl, Br, CN, CF_3, SO_3H, COOH, COC_6H_5, SO_2Alkyl, COOAlkyl or $CONR^1R^2$), are similarly used. C.O.C.

Titanic and Zirconic Acid Esters as Water-repellent Finishes for Textiles
Arthur J. Dickinson *BP* 786,444

The 3:5:5-trimethyl hexanol-1 esters of titanic and zirconic acids are stable to moisture present in the fibres, are readily hydrolysed by steaming and pressing of the impregnated material and the alcohol liberated by hydrolysis is readily dried off from the fibres. C.O.C.

Quaternary Phosphonium Polyphosphates as Water-repellent Agents and Insecticides
ICI *BP* 786,902

Quaternary phosphonium polyphosphates containing linear groups of $(\overline{PO_3})^-$ units, each unit being associated with a cation, the greater proportion of these cations being quaternary phosphonium cations in each of which the 4 valences of the P ion are attached to organic radicals, e.g. acetyl tripropyl phosphonium polyphosphate, can be used to impart a water-repellent finish to textiles or glass or as insecticides. C.O.C.

Titanium and Zirconium Organic Compounds soluble in both Water and Organic Solvents
National Lead Co. *BP* 786,388

Esters of orthotitanic or orthozirconic acid with an amino alcohol of formula $HO{\cdot}R^1{\cdot}NR^3{\cdot}R^2{\cdot}NR^3{\cdot}R^4$ (R^1 = ethylene or alkyl-substituted ethylene; when R^2 = a divalent alkylene of 1–3 C then R^3 = H, β-hydroxyalkyl or β-aminoalkyl and R^4 = β-hydroxyalkyl or β-aminoalkyl; when R^2 = $CH_2{\cdot}CH_2{\cdot}NX{\cdot}CH_2{\cdot}CH_2$ then R^3, R^4 and X = H or β-hydroxyalkyl), e.g. the product obtained from 1 mol. of *NNN'N'*-tetrakis(2-hydroxypropyl) ethylene diamine and 2 mol. of tetra*iso*propyl orthotitanate, are useful as dispersing agents, for adding to paints to improve the durability and hardness of the coatings produced, for treating textiles, etc. C.O.C.

Tin or Zirconium Compounds as Catalysts for Curing Silicones
Carlisle Chemical Works *BP* 787,175

Chelates of tin or zirconium or organic zirconium salts used as catalysts for curing silicones neither act too quickly nor too slowly and silicone preparations containing them can be stored for long periods without loss in efficiency. C.O.C.

Water-repellent Finish
Crown Chemical Corpn. *USP* 2,750,306

The product obtained by treating a compound of formula $R{\cdot}CONH{\cdot}CH_3$ (R = paraffin hydrocarbon of 9–21 C) with a straight chain alkyl nitrile (Alk of 10–22 C), then with HCHO and HCl and finally with pyridine or C-alkyl substituted pyridine is made into an aqueous dispersion. Cellulosic, protein, cellulose ester, polyamide, polyacrylic or polyester fibres impregnated with this dispersion, dried and baked are given a water-repellent finish fast to laundering and dry cleaning. C.O.C.

Water-insoluble Phosphates of Basic Organic Condensates as Flame-resisting Agents
FBy *BP* 786,736

Modification of *BP* 648,883 (*J.S.D.C.*, **67**, 203 (1951)). By adding the phosphoric acid after the N compound and aldehyde have been condensed, products are obtained which are water-insoluble without further curing. Such products are suitable for adding to cellulose fibres in the beater or they may be formed *in situ*, e.g. cotton cloth is first impregnated with a dicyandiamide-formaldehyde condensate, then treated with 10% aq. Na or NH_4 metaphosphate and finally dried at 100°C. C.O.C.

Plastisol Compositions for producing Coatings and Films Permeable to Water Vapour
DuP *BP* 788,560

A plastisol yielding a water vapour-permeable film comprises a particulate polymer blend of (*a*) a water-insoluble, water-dispersible, non-electrolyte, film-forming polymer of an ethylenically unsaturated monomer, and (*b*) an aqueous-gel-forming, cross-linked polyelectrolyte polymer containing 1:2-epoxide groups and $\not<$ 0·2 acidic groups per 100 mol.wt.; (*a*) and (*b*) have been dispersed in a common aqueous medium and simultaneously separated to form a dry particulate polymer which is then dispersed in an organic liquid plasticiser which is a non-solvent for (*a*) at room temperature but which dissolves it on heating. C.O.C.

2:2'-Dihydroxy-4:4'-substituted Benzophenones for Preserving Coloured and Non-transparent Organic Substances
General Aniline *BP* 786,762

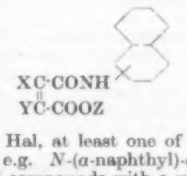
2:2'-Dihydroxy-4:4'-substituted benzophenones, whose 4 and 4' substituents are either hydroxy or alkoxy, are compatible with many types of coloured and non-transparent materials to yield ultraviolet radiation absorbing compositions. Their efficiency at 400 $m\mu$ is about twelve times that of hitherto known stabilisers against ultraviolet radiation. C.O.C.

Ultraviolet Absorbing Agents
Eastman Kodak Co. *USP* 2,748,021

The products formed by condensing α-methyl-α-phenyl hydrazine with an aldehyde, e.g. 4-methoxy-3-sulphobenzaldehyde sodium salt, are absorbers of high molecular extinction and high stability with respect to fading caused by ultraviolet radiation. C.O.C.

Fungicidal Composition especially suitable for use in Paints
Ethyl Corpn. *USP* 2,749,269

Compounds of formula—



(X and Y = H or Hal, at least one of them being Hal; Z = H or Alk), e.g. *N*-(*α*-naphthyl)-*α*-chloromaleamic acid, are fungicidal compounds with a wide range of uses but which are especially suitable for use in paints or other coating compositions. C.O.C.

Fungicidal Composition
Pennsylvania Salt Manufacturing Co. *USP* 2,749,268

A mixture of a surface active agent and a compound of formula $Ar^1{\cdot}CO{\cdot}COR{:}CH{\cdot}CO{\cdot}AR^2$ (Ar^1 and Ar^2 = phenyl, biphenylyl, triphenylyl or naphthyl and may contain as substituents 1–3 Hal or Alk of 1–5 C; R^2 a primary or secondary Alk), e.g. 1:4-diphenyl-2-methoxy-2-butene-1:4-dione, is an excellent fungicide for use on textiles, leather, etc. C.O.C.

Synthetic Tanning Agents
FBy *BP* 787,347

Solid, light-coloured, soluble condensates having excellent tanning properties are obtained by mixing sulphite waste liquor treated with caustic alkali with condensates

of aromatic sulphonic acids and aromatic hydroxy compounds or similar condensates and then precipitating the resulting water-soluble with a mineral acid. C.O.C.

New Products developed since November 1956— Alphabetical List (IV this page)
Rendering Thermoplastic Materials Faster to Light (XIII p. 216)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

New Products developed since November 1956— Alphabetical List

Amer. Dyestuff Rep., **46**, 891–919 (2 Dec.); 1008–1009 (30 Dec. 1957)

Colour and Structure of Organic Compounds

M. Koizumi

Kagaku (Science), **27**, 118–125 (1957): *Chem. Abs.*, **51**, 14531 (10 Oct. 1957)

Review, 25 references. C.O.C.

Synthesis of Naphthalene-1-sulphinic-7-sulphonic Acid and Naphthalene-1:7-disulphonic Acid

W. Lisowski

Przemysl Chemiczny, (12), 697–700 (1956): *Polish Tech. Abs.*, (27), 73 (1957)

Diazotisation of 1:7-naphthionate was modified to conform to the conditions of a pilot-plant process. Three possibilities were investigated concerning the successive introduction of reagents into the reaction resulting from substituting the diazo group by the sulpho group. It was found that the best method under the conditions of the pilot-plant process is the simultaneous introduction of sulphurous anhydride and of sodium diazonaphthionate. A description is included of the method of purifying the sodium salt of naphthalene-1-sulphinic-7-sulphonic acid, and a discussion of the method of oxidising that salt to naphthalene-1:7-disulphonic acid by using hydrogen peroxide or by applying sodium permanganate in slightly alkaline medium. C.J.W.H.

2:3-Derivatives of Naphthalene. III— Electrophilic Substitution Reactions of 3-Nitro-2-naphthylamine and *N*-Acylated Derivatives

E. R. Ward, T. M. Coulson, and P. R. Wells

J.C.S., 4816–4823 (Dec. 1957)

Diazo coupling, chlorination, bromination, and nitration of 3-nitro-2-naphthylamine and several of its *N*-acyl derivatives are described; it is found that nitro groups can be introduced at the 1-, 5-, 6-, or 8-position. Some general features of electrophilic substitution in naphthalene deriv., in contrast to that in benzene deriv., are discussed. Diazo-naphthol formation by a variety of 1-substituted 3-nitro-2-naphthylamines and 1:3:*x*-trinitro-2-naphthylamines always occurs by nucleophilic displacement of a group at the 1-position, forming a 1:2-diazo-naphthol; this confirms the apparent impossibility of forming a 2:3-diazo-naphthol structure. 1:6:7-Trinitronaphthalene, prepared by a diazo decomp. from either 3:5- or 3:8-dinitro-2-naphthylamine, is found to be identical with the mononitration product of 2:3-dinitronaphthalene. H.H.H.

Oxidation of Aromatic Amines. V— Oxidation by Perphosphoric Acids

E. Boyland and D. Manson

J.C.S., 4689–4694 (Dec. 1957)

These oxidations have been studied (*a*) because of possible analogy with biological oxidation, (*b*) as a method of preparation of the aminophenyl phosphates, and (*c*) for comparison with oxidation by persulphate (cf. *J.C.S.*, 3623 (1953)). Oxidation by permonophosphoric acid, or a mixture of peracetic and phosphoric acids, converts aniline to *p*-aminophenol and *p*-aminophenyl dihydrogen phosphate, and 2-naphthylamine to 2-amino-1-naphthol and 2-amino-1-naphthoyl dihydrogen phosphate, whereas *NN*-dimethyl-2-naphthylamine gives its *N*-oxide, and anthranilic acid yields azoxybenzene-2:2′-dicarboxylic and 5-hydroxyanthranilic acids. The oxidation to phenolic deriv. does not proceed in neutral or alkaline soln., or in the absence of acetone or some other carbonyl deriv. H.H.H.

Aromatic Azo and Diazo Compounds. XXV— Synthesis of Polyazo Direct Blue (C.I. 34200)

Z. J. Allan and J. Podstata

Chem. Listy, **51**, 1142–8 (1957): *Chem. Abs.*, **51**, 15479 (25 Oct. 1957)

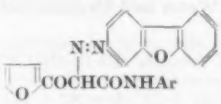
Improvements in the method of making Sirius Supra Blue G (C.I. 34200) are described. Two unknown reactions were discovered: easy hydrolysis of the NH_2 group with azo dyes derived from 1-naphthylamine (I) and an unusual mode of decomposition of the corresponding diazo compounds. When diazotised aniline-2:5-disulphonic acid (II) (2·5 millimoles) is added at 0°c. during 15 min. to Na salt of 1-naphthylamine-7-sulphonic acid (III) (2·625 millimoles) in presence of $NaHCO_3$ (0·3 equivalent), the yields are raised 2% on the average. The azo dye II → III is hydrolysed by dil. HCl or acetic acid within several days at 20°c. to the trisodium salt of 2:5-disulphophenyl-4-azo-1-naphthol-7-sulphonic acid. Analogous dyes are similarly hydrolysed, some of them much quicker. The second coupling in synthesising C.I. 34200 is done at 0°c. by using the free base of I (10 millimoles) suspended with glue (0·2 g.) and Neokal (0·03 g.) in water (6·6 ml.) and yields a mixture of dyes. The precipitate obtained by salting out contains only the monoazo dye III → II. The disazo dye II → III → I is unstable and splits off the NH_2 when dried at 80°c. to yield the diazo dye II → III → 1-naphthol. The 3rd coupling (with 2-phenylamine-5-naphthol-7-sulphonic acid) gives the highest yields of C.I. 34200 (61·7%) when carried out in ammonia at 3°c.; 6 by-products are obtained which were partially identified. C.I. 34200 is purified by dissolving the crude Mg salt (40 g.) in water (1 litre) at 90°c. with addition of the necessary 2·5 N-Na_2CO_3, treating the solution with carbon (10 g.) and silica (10 g.), filtering, acidifying at 50°c. with acetic acid (6 ml.), precipitating with a solution of $MgCl_2$, $6H_2O$ (13 g.), and washing with water. The mechanism of the formation of C.I. 34200 is discussed. Most of the coloured by-products are formed by decomposition of the diazotised disazo dye II → III → I; replacement of the diazo group by OH, usual in the decomposition of common diazo compounds, occurs to 7–10% in the dye II → IV → I solely in acid medium, the main product of decomposition being a yellowish brown dye of unknown composition and low R_f. Similar behaviour is shown by other dyes derived from 1-naphthylamine. C.O.C.

Monoazo Dyes from Furoylacetarylides and Dibenzofuran. III

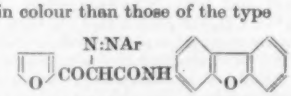
A. Cerniani and G. Cordella

Ricerca sci., **26**, 2721–5 (1956): *Chem. Abs.*, **51**, 15951 (25 Oct. 1957)

Dyes of the type



are deeper in colour than those of the type



but are less fast to washing. Preparation of a number of such dyes is described. C.O.C.

Azoic Dyes by use of Furoyl Coupling Components. V

A. Cerniani and G. Cordella

Ricerca sci., **26**, 3352–6 (1956): *Chem. Abs.*, **51**, 15133 (10 Oct. 1957)

Syntheses of twenty-three azoic dyes of the types N - aryl - *α* - dibenzoselenophene - 2 - ylazo - *β* - oxo - 2 furanpropionamide, *N* - aryl - *β* - oxo - *α* - [*p* - (phenylthio) - phenylazo] - 2 - furanpropionamide, *α* - (arylazo) - *β* - oxo - 4′-(phenylthio) - 2 - furanpropionanilide and *α* - (arylazo) - *N* - dibenzothiophene - 3 - yl - *β* - oxo - 2 - furanpropionamide S_1S-dioxide are given. They are achieved (1) by coupling the 3-aminodibenzoselenophenone and 4-aminodiphenyl sulphide with various furoyl acetarylides or (2) by coupling the diazonium salts of aromatic amines with the furoyl acetarylides of 4-aminodiphenylsulphide or of 2-aminodibenzothiophene sulphone. The fastnesses of the dyes are given. C.O.C.

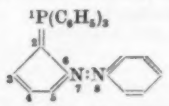
The Yellow Components and the use of the Benzidine Group as a Separating Component in the Synthesis of Azo Dyes
I. Reichel and R. Palea
Acad. rep. populare Romine, Baza cercetari stiint, Timisoara, Ser. stiinte chim., **3**, No. 1/2, 33–55 (1956): *Chem. Abs.*, **51**, 18613 (25 Nov. 1957)

Attempts were made to prepare green dyes by intermolecular mixing of yellow and blue components using "separating components", i.e. atoms or groups which tend to block the movement of π electrons. Thus tetrazotised benzidine (I) or its 2:2′-disulphonic acid was coupled with the monoazo compound (II) *p*-nitroaniline → H acid followed by coupling with phenol, 3-methyl-1-phenyl-5-pyrazolone (III), etc. The dye from I, II, and III gave khaki on cotton. E.S.

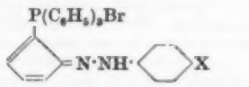
Phosphinemethylenes. III— A New Class of Azo Dyes containing Phosphorus
F. Ramirez and S. Levy
J. Amer. Chem. Soc., **79**, 6167–6172 (5 Dec. 1957)

Triphenylphosphoniumcyclopentadienylide, (I)

couples readily with diazonium salts to yield brilliant azo dyes. Coupling occurs at a position in the 5-membered ring which preserves the stable *cyclo*pentadienide system and gives rise to the longest of the possible conjugated systems terminating at a P atom. Thus with benzenediazonium chloride and *p*-nitrobenzenediazonium chloride, the dyes triphenylphosphonium-(2-phenylazo)-*cyclo*pentadienylide,



and triphenylphosphonium-[2-(*p*-nitrophenylazo)-*cyclo*pentadienylide] respectively are obtained. Their ultraviolet and infrared spectra and dipole moments are described. With hydrobromic acid these dyes yield phenylhydrazones of a simple phosphonium derivative of *cyclo*pentadienones, viz.,



(X = H or NO_2 as the case may be). I is obtained in yields comparable to those obtained by phosphine is added to the mixture of dibromides resulting from *cyclo*pentadiene and Br in chloroform, by treating pure *cis*-3:5-dibromo*cyclo*pentene with triphenylphosphine and then with alkali. C.O.C.

Optical Properties of some Dyes in a "Massive" State by the Mirror Reflection Method
N. N. Pribytkova and L. S. Agroskin
Optika i Spektroskopiya, **2**, 628–632 (1957): *Chem. Abs.*, **51**, 16096 (10 Nov. 1957)

Refractive indices and absorption coefficients (x) of cyanine (I), Brilliant Green, Malachite Green, Brilliant Violet and Rhodamine B (II) were determined by the mirror reflection method. The spectra and x, n curves were complex and peculiar to each dye. In general, x curves showed 2 maxima, the relative intensity of which for I and II decreased during actinic illumination, the short wave maximum decreasing the quicker. Use of the mirror reflection method for studying the light absorption of dyes and their fading on exposure to sunlight, heat, humidity, etc., is briefly discussed. C.O.C.

Pyrrole Dyes. VI. Tripyrrylmethenes
A. Treibs and K. Hintermeier
Ann., **605**, 35–42 (1957): *Chem. Abs.*, **51**, 14672 (10 Oct. 1957)

Excellent yields of tripyrrylmethenes are obtained by condensing substituted pyrroles with pyrrole acid chlorides or dipyrryl ketones and $POCl_3$. Thus (2:4-dimethyl-5-carbethoxy-3-pyrryl)bis(2:4-dimethyl-3-carbethoxy-5-pyrryl)methene is obtained from 2:4-dimethyl-3-carbethoxy pyrrole and 2:4-dimethyl-5-carbethoxy-3-carbo-*tert.*-butoxy pyrrole. C.O.C.

Synthesis of Polycyclic Aromatic Compounds. I— Reaction of Quinones with Vinylnaphthalenes and Related Dienes
W. Davies and Q. N. Porter
J.C.S., 4967–4970 (Dec. 1957)

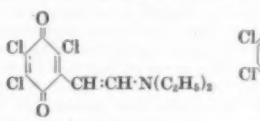
A high yield of chrysene-1:4-quinone (I) is obtained when 1-vinylnaphthalene (II) reacts with excess of *p*-benzoquinone; when excess of II is used, an adduct is formed which is easily dehydrogenated by benzoquinone or chloranil to chrysene-3:6-quinone. II also reacts with 1:4-naphthaquinone to give naphtho(2′:1′-1:2)anthracene-9:10-quinone (III). Reduction of I by $LiAlH_4$ gives directly 3:4-benzophenanthrene, while III reduces with Zn dust in acetic anhydride to 9:10-diacetoxynaphtho(2′:1′-1:2)-anthracene, and with Sn_2Cl_6 in conc. HCl to the anthrone, which subsequently gives naphtho(2′:1′-1:2)anthracene with Zn dust and NaOH under toluene. 2-Vinylnaphthalene gives 3:4-benzophenanthrene-1′:4′-quinone with *p*-benzoquinone, which reduces directly to 3:4-benzophenanthrene with $LiAlH_4$, but with 1:4-naphthaquinone it affords only 2:2′-dinaphthyl-1:4:1′:4′-diquinone. The one-stage reduction of quinones to hydrocarbons by $LiAlH_4$ fails except when the quinone grouping is on the outermost ring. H.H.H.

Synthesis of Substituted Amino-, Aminovinyl-, and Aminobutadienyl-*p*-quinones
D. Buckley, H. B. Henbest, and P. Slade
J.C.S., 4891–4900 (Dec. 1957)

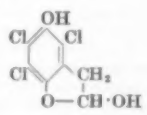
It is found that dialkylaminovinylquinones can often be synthesised in good yield from halogenated quinones, acetaldehyde, and secondary amines, isolation of the enamines being unnecessary. Also, a dialkylaminobutadienyl quinone has been prepared in the naphthalene series by using 1-diethylaminobutadiene or, less efficiently, a mixture of diethylamine and crotonaldehyde. Replacement of chlorine in the blue dialkylaminovinyltrichlorobenzoquinones may lead to purple or green cpd. For comparison, some reactions between quinones and primary and secondary amines are described, and the light-absorption properties of the coloured products discussed; it is considered that the side-chains $(CH=CH)_{1-2}\cdot NR_2$, in the new quinones are of *trans*-geometry. H.H.H.

Amine Oxidation. II— Reactions of Aliphatic Tertiary Amines with Quinones. Detection of Dehydrogenation by the Formation of Coloured Dialkylaminovinylquinones
D. Buckley, S. Dunstan, and H. B. Henbest
J.C.S., 4880–4891 (Dec. 1957)

This and the following papers deal with the oxidation of *tert.* amines by organic oxidising agents, which often occurs at room temp. Reactions between *tert.* amines containing a flexible $\rangle N\cdot CH\cdot CH\langle$ grouping and some halogenated quinones can result in dehydrogenation to enamines $\rangle N\cdot C{:}C\langle$. If the enamine contains a β–CH grouping, coupling with a second mol. of halogenated quinone can occur, to give a blue or purple dialkylaminovinylquinone (e.g. the blue cpd. I). For isolation of coloured quinones, the two-stage reaction proceeds best with simple *N*-ethyl cpd. Catalytic hydrogenation of I gives a colourless lactol (II), which oxidises with chromic acid in acetone to give the yellow high-melting cpd. III.



(I)



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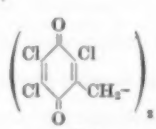


(III)

H.H.H.

Structure of the Primary Condensate in the Koenig Dye Synthesis
S. Creyf and L. Roosens
Mededel. Vlaam. Chem. Ver., **19**, 1–11 (1957): *Chem. Abs.*, **51**, 16303 (20 Nov. 1957)

The ultraviolet absorption spectrum of the condensate (I) of nicotinamide and BrCN has maxima at 265 and 346 mμ at pH 9 in water, while the maximum of 4(1*H*)-pyridone in sodium ethoxide is at 250, of *N*-methyl-2-oxonicotinamide at 220 and 322, of NaOCH:CHCH:CHCHO at 365, of 5-(2:4-dinitrophenylamino)-2:4-pentadienal at 350 with a shoulder at 400, of 5-(2-furyl)-2:4-pentadienal at 346 (log ε 4·47), and of 2:4-hexadienal at 271 mμ (log ε 4·43). It seems that I is not a *N*-cyanopyridone but the salt of an open-chain compound, $NCNHCH{:}CHCH{:}C(CONH_2)CHO$, which is formed by opening the ring in the 1:2-position and tautomerisation. > 40 references. C.O.C.

Relationship between Colour, Constitution, Solvents and Chemical Reactivity. Pyridine $N^{\oplus}N^{\ominus}$-betaines
K. Dimroth, G. Arnoldy, S. von Eicken, and G. Schiffler
Ann., **604**, 221–251 (1957): *Chem. Abs.*, **51**, 16467 (20 Nov. 1957)

The contradictory intensification of the deeply coloured, supposedly tautomeric anhydrobases ("phenylarylimines") (I) (2:4:6-R,R‴,R″$C_5H_2N^{\oplus}N^{\ominus}$R′) of Schneider (*Chem. Abs.*, **36**, 4820 (1942)) in non-polar solvents and other obscurities have been reinvestigated chemically and physically because numerous non-tautomeric dyes show pronounced "solvatodiomy" (John, *Chem. Abs.*, **42**, 4498 (1948)) brought about by mesomeric shifts caused by reciprocal reaction with the solvent. It has been proved that I are not tautomeric systems of two or more compounds but rather individual compounds to which only the polar form of two constitutional structures can be assigned. C.O.C.

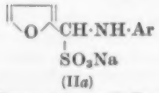
Action of Sodium Sulphite on Stenhouse Dyes
J. C. McGowan and F. M. Page
Chem. and Ind., 1648 (21 Dec. 1957)

Stenhouse dyes (I), when warmed on the water-bath with aq. sodium sulphite, react according to the scheme—

$$\underset{(I)}{Ar{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}C(OH){\cdot}CH{:}NH{\cdot}Ar\}^{+}Cl^{-}} + Na_2SO_3 \downarrow$$

$$Ar{\cdot}NH_2 + Ar{\cdot}C_5H_5{\cdot}SNO_4Na + NaCl$$
$$\underset{(II)}{}$$

Possible structures for II are II*a* and II*b*, and experiments are described which favour II*b*.



(II*a*)

$$Ar{\cdot}N{:}CH{\cdot}C(OH){:}CH{\cdot}CH{:}CH{\cdot}SO_3Na$$
(II*b*)

H.H.H.

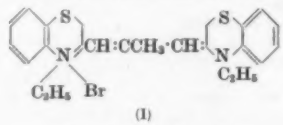
Structure of Sensitising Dyes adsorbed on Silver Halide Crystals

I— Cyanine Dyes on Silver Iodide
S. Sonoike and H. Okabe
Ôyô Butsuri, **26**, 392–7 (1957)

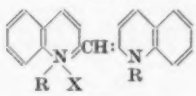
Electron diffraction studies of cyanine dyes adsorbed on AgBr showed that only Cyanine Blue was adsorbed in multimolecular layers. Two types of diffraction were observed, one having well defined peaks and the other only halves. After the dyes were removed with ethanol or butanol, only the patterns corresponding to AgI were seen. This indicates that the AgBr is converted to AgI by reaction with the dye so that the dye is adsorbed not on AgBr but on AgI. The observed spacings for the adsorbed dye were not different from those of AgI by 72–3%. The stable adsorption was on the (100) face of AgI, but adsorption on the (001) face was also noticed but was less significant. The dye molecules were so oriented on the surface that the side spacing is equal to the spacing 4·59A of AgI and the dye molecules are tilted by about 30° from the normal to the surface. A model arrangement is shown.

II— Cyanine Dyes on Silver Bromide and Chloride
Ibid., 397–402

Dye I on AgBr has the spacing 6A and the molecules are aligned along the spacing 5·75A of AgBr with their axes at 40° to the substrate. Dye II, when R = CH_3 and X = R, has the spacing 4A and accommodates the spacing 4·06A of



(I)



(II)

AgBr with an angle 60°. Dye II, when R = C_2H_5 and X = C, has the spacing 4·3A on AgCl and has either a fibrous orientation or its own crystal structure. Presumably the arrangement of adsorbed molecules is regular when the adsorption face is strong and tends to become random as the face becomes weaker. C.O.C.

Fluorescence of Disodium Salt of 4:4′-Diaminostilbene-2:2′-disulphonic Acid and Blancophor A
S. Bartkowicz
Zesz. Nauk. Politech. Lodz., No. 15 (*chemia* 5), 17–20 (1957)

The disodium salt of 4:4′-diaminostilbene-2:2′-disulphonic acid exhibits fluorescence, the maximum of which is found at 4350A, whilst that of Blancophor A is at 4100A. The order of intensity of the fluorescence of Blancophor A is two degrees higher than that of the intermediate. T.Z.W.

Fluorescent Derivatives of 1:2:3-Triazole

Introductory Remarks
V. H. Hanousek and J. Dobáš
Chem. Listy, **51**, 1101–2 (1957)

The aim of the work was to prepare fluorescent brightening agents which absorb light of 320–80 mμ and emit it as blue. The triazole ring makes them substantive to cellulose.

I— Sulphonated bis(Naphthotriazoles) derived from *p*-Phenylenediamine, Benzidine, Benzidine Sulphone and Diaminodiphenylurea
J. Dobáš, J. Pirkl, and V. Hanousek
Ibid., 1103–1112

Preparation, optical and spectral properties of these compounds are given. Their relative substantivity determined by chromatography on paper in the system 1% NaCl in 5% aq. pyridine is expressed by R_g, the ratio between the distances of the spots of the respective compounds and that of the standard (R_g 1) from their original positions. The R_g for eight compounds is given as well as their ultraviolet spectra.

II— Sulphonated Benzo- and Naphtho-triazoles derived from 4:4′-Diaminostilbene-2:2′-disulphonic Acid
Ibid., 1113–1121

The triazole ring is a chromophore whose effect can be compared with that of CO and CH:N groups. Experiments with models show that the triazole substituted in position 2 is the bearer of visible fluorescence whereas the 1-substituted ring is not fluorescent in the visible region. Preparation of a large number of compounds is described, but only Na 4:4′-bis(2-naphtho[1,2]triazolyl)stilbene-2:2′:6″:6‴-tetrasulphonate is of use as a fluorescent brightening agent. The ultraviolet spectra and fastness to light of the compounds listed is given.

III— Sulphonated Naphthotriazoles derived from 4-Aminodiphenyl
Ibid., 1122–6

Derivatives of 2-xenylnaphtho[1,2]triazole containing no sulpho group in the xenyl residue in *o*-position to the triazole ring, are good fluorescent brightening agents for cellulose. The unfavourable influence of this group can be partly compensated by introducing certain acylamino groups into the *p*-position in the xenyl residue. Dependence of the optical properties and substantivity on the chemical constitution and planar structure is discussed. Preparation of 11 compounds is described of which Na 2-xenylnaphtho[1,2]triazole-4″:6(?) disulphonate and

Na 2-(4″-methoxyxenyl)naphtho[1,2]triazole-6:8-disulphonate are very good; Na 2-(xenylnaphtho[1,2]triazole-6:8-disulphonate, Na, 2-(4″-chloroxenyl)naphtho[1,2]triazole-6:8-disulphonate, and the *p*-methoxy benzoyl derivative of Na 2-(4″-aminoxenyl)naphtho[1,2]triazole-3′:6-disulphonate are good fluorescent brightening agents. The acetyl, phenylacetyl and phenoxy acetyl derivatives of Na 2-(4″-aminoxenyl)-naphtho[1,2]triazole-3′:6-disulphonate noticeably brighten cotton, while the parent compound and Na 2-xenylnaphtho[1,2]triazole-3′:6-disulphonate have a negligible brightening effect.

IV— Colour and Fluorescence of some Derivatives of 2-Phenylnaphtho[1,2]triazole

Ibid., 1127–1135

Changes in colour and fluorescence were brought about by substituting NH_2 and OCH_3 groups in the 2′, 3′ and 4′ position and with sulpho groups in the same positions or in 4–8 positions of 2-phenylnaphtho[1,2]triazole. The changes in colour obtained are less than those produced by the same substituents in other chromogenic systems. The changes in fluorescence are parallel to those in colour with the exception of compounds substituted by an NH_2 group in position 3′. Preparation of 21 compounds is given.

V— Acyl Derivatives of 2-(3′- and 4′-aminophenyl)-naphtho-[1,2]triazolesulphonic Acids

Ibid., 1136–1141: *Chem. Abs.*, **51**, 15502–9 (25 Oct. 1957)

13 compounds of this type were prepared and the dependence of their colour and fluorescence on constitution is compared with that of some of the agents described in previous parts of this paper. Na-2-[4′-(4″-amino-6″-hydroxy-2″-triazinylamino)phenyl]naphtho[1,2]-triazole-6-8-disulphonate is a very good fluorescent brightening agent for cellulose but has poor fastness to light.

C.O.C.

Spectroscopically Demonstrable Electron States of the Stable and Metastable Molecules of some Acridine Dyes and of Fluorescent Cations

V. Zanker and E. Miethke

Z. Naturforsch., **12a**, 385–395 (1957): *Chem. Abs.*, **51**, 16109 (20 Nov. 1957)

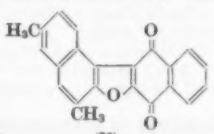
The low-temperature spectrum of the univalent cations of 3:6-diaminoacridine, 9-phenyl-3:6-diaminoacridine, 3:6-bis(dimethylamino)acridine and fluorescein have been studied in the 4000–50,000 cm^{-1} range in alcohol–ether solution. The stable singlet and the energy richer metastable triplet terms were determined. With dye cations the triplet transition with the longest wavelength lies in the region 7900–9100 cm^{-1}. The spectroscopic data are tabulated and term schemes given for 3:6-diaminoacridine and 9-phenyl-3:6-diaminoacridine. C.O.C.

Polymethylated Homologues of 3:4-Benzacridine and 3:4-Benzocarbazole and Related Compounds

Ng. Ph. Buu-Hoï, P. Jacquignon, and C. T. Long

J.C.S., 4994–4997 (Dec. 1957)

The synthesis is reported of several penta- and hexamethyl-3:4-benzacridines, dimethyl-3:4-benzocarbazoles, and tetra- and penta-methyl homologues of 10-chloro-5:10-dihydro-1:2-benzophenarsazine. Convenient intermediates for these syntheses are the dimethyl-2-naphthols, some of which are now thoroughly investigated. 3:6-, 3:7-, and 6:7-Dimethyl-2-naphthols have been prepared from 2:6-, 2:7-, and 2:3-dimethylnaphthalene via the sulphonic acids, and found to condense readily with 2:3-dichloro-1:4-naphthaquinone (I) giving brasanquinones (e.g. II). 3:7- and 4:7-Dimethyl-1-naphthols were prepared from 2:6- and 1:6-dimethylnaphthalene-4-sulphonic acids respectively, and reacted with I to give brasanquinones.



(II) H.H.H.

Organic Semiconductors with High Conductivity. II— Structural Aspects of the Violanthrene–Iodine Complex

H. Akamatu, Y. Matsunaga, and H. Kuroda

Bull. Chem. Soc. Japan, **30**, 618–625 (Sept. 1957)

In the molecular compound between violanthrene and iodine the molecular ratio is approx. 1:2. The violanthrene–iodine system is a solid soln. between the complex and either iodine or violanthrene, whichever is in excess. Radial-distribution analysis of the complex shows the interatomic distance of iodine to be increased from 2·67 to 2·85A. The complex is supposed to have a structure in which I_2 molecules are sandwiched between neighbouring violanthrene molecules. The system as a whole is amorphous and resembles the molecular compounds of graphite. A.J.

Reversible Oxidation of Phthalocyanines

C. J. Pedersen

J. Org. Chem., **22**, 127–132 (1957): *Chem. Abs.*, **51**, 14753 (10 Oct. 1957)

Phthalocyanines (I) can be reversibly oxidised in non-aqueous media to substances soluble in organic solvents and from which I can be regenerated by reduction. Thus α-Cu phthalocyanine (II) treated with benzoyl peroxide in ethanol yields the compound $C_{90}H_{24}CuN_8O_2$, a 5:21-methoxy(benzoyl) addition compound (III) of II. Cu-free II and the Mg, Zn, Fe, Co and Ni salts are also reversibly oxidised, but perchlorinated II resists oxidation. I reacts more readily in the α than in the β form. The oxidation products are stable in absence of reducing agents, they do not melt, but at 140–220°C. they are converted to I. Reducing agents regenerate I which are always obtained in the α form. C.O.C.

Advances in Phthalocyanine Technology

R. E. Brouillard

Amer. Ink Maker, **35**, (3), 36–40, 73 (1957): *Chem. Abs.*, **51**, 15965 (25 Oct. 1957)

A discussion of the metal phthalocyanines and particularly of Cu phthalocyanine, C.I. 74160. When this pigment produced by acid pasting is dispersed in some organic liquids the α form is converted to the β form and the larger particles increase in size at the expense of the much smaller ones. This "Ostwald ripening" is prevented by the much narrower range of particle sizes produced by grinding the pigment with an extractable grinding assistant, e.g. NaCl, and the organic liquid. Small amounts of certain other phthalocyanines and also substitution of Cl exclusively in the 5- or 4-position render the pigment stable in organic liquids. This is explained with the aid of diagrams of molecular spatial arrangements which show that the substitutions prevent the shift in molecular arrangement from the α form, which does not form large crystals, to the normally stable β form. C.O.C.

Phthalocyanine Derivatives. V— Salts of Iron Phthalocyanine-4-sulphonic Acid

N. Kukada

Nippon Kagaku Zasshi, **76**, 1378–1381 (1955): *Chem. Abs.*, **51**, 17945 (25 Nov. 1957)

The following salts of ferrous and ferric phthalocyanine-4-sulphonic acids were prepared from urea, 4-sulphophthalic acid and $FeCl_2$ or $FeCl_3$:trihydrogen monosodium, dihydrogen disodium, monohydrogen trisodium tetrasodium, trihydrogen monobarium, monohydrogen tribarium and tetrabarium. The ferrous and ferric compounds formed at the same time are separated by the different solubilities in conc. HCl and 80% ethanol, ferrous compounds being the less soluble. Both the ferrous and ferric compounds decompose H_2O_2. C.O.C.

Phthalocyanine Pigments and their Sulphonated Derivatives

I. Rusznák, E. Marton, I. Sello, and G. Szoke

Magyar Textiltechnika, (9), 325–327 (1956): *Hungarian Tech. Abs.*, **9**, (3), 90 (1957)

By sulphonating phthalocyanine a direct dye can be obtained, easily soluble in cold water and in dilute soda solutions. The experiments verified that metal atoms form bivalent complex compounds. Tervalent metals bind mobile halogen atoms with their third valency. In a more advanced stage of sulphonation a vattable dye is obtained which is substantive to cellulose, and later a direct dye is reached. The experimental part deals with the sulphonating process. C.J.W.H.

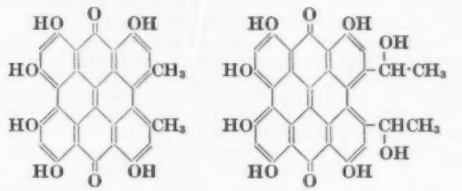
Photodynamically Active Plant Pigments

H. Brockmann

Proc. Chem. Soc., 304–312 (Nov. 1957)

The colouring matter hypericin (I) makes animals subject to photogenic injury (hypericism) by sunlight when they have eaten genus *Hypericum*. Its constitution (I) has

been established by a new spectroscopic method for the elucidation of the basic structure of polycyclic aromatic hydroxyquinones (cf. Brockmann and Budda, *Chem. Ber.*, **86**, 432 (1953)), and also confirmed by synthesis. During the examination of 22 species of *Hypericum* plants, a second pigment, *pseudo*hypericin (II), was separated which produces photodynamic effects like I. It is pointed out that all the hitherto known photodynamically active plant pigments are 4:5:7:4′:5′:7′-hexahydroxy deriv. of helianthrone or naphthodianthrone; they are synthesised in the plant by dehydrogenation of correspondingly substituted anthrones or anthronols, and are distinguished first by their 2- and 2′-substituents, and secondly by their mode of combination and the chemical nature of the colourless residues.



(I) (II)

H.H.H.

Mangiferin, the Colouring Matter of Mango (*Mangifera indica* Linn)

S. Iseda

IV—Isolation of 1:3:6:7-Tetrahydroxyxanthone and the Skeletal Structure of Mangiferin

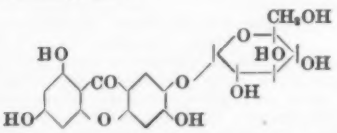
Bull. Chem. Soc. Japan, **30**, 625–629 (Sept. 1957)

Mangiferin ($C_{19}H_{18}O_{11}$) on heating in phenol with HI or HBr yields a crystalline product, shown to be 1:3:6:7-tetrahydroxyxanthone. Evidence is adduced that the xanthone skeleton is not produced during the reaction with HI and must therefore be present in the original pigment.

V—Identification of the Sugar Component and the Structure of Mangiferin

Ibid., 629–633

Mangiferin is decomposed by heating with dil. H_2SO_4 at 140°C. with the liberation of glucose. From infrared spectral data and other evidence it is concluded that an α-D-glucopyranoside residue is attached to the 7-position of the xanthone skeleton. The following structure is proposed for mangiferin—



A.J.

Cercosporin. A Pigment of *Cercosporina Kikuchii Matsumoto et Tomoyasu*. I—Cultivation of Fungus, Isolation and Purification of Pigment

S. Kuyama and T. Tamura

J. Amer. Chem. Soc., **79**, 5725–6 (5 Nov. 1957)

A red pigment, cercosporin, is obtainable in good yield from the mycelia of *C. Kikuchii*. Its empirical formula is $C_{30}H_{28}O_{10}$ and it contains two methoxy and several acidic hydroxyl groups, and has a quinonoid structure. Its alkaline solutions are green and the leuco compound is bright yellow with intense green fluorescence.

II—Physical and Chemical Properties of Cercosporin and its Derivatives

Ibid., 5726–9

Several acetyl and methyl derivatives of the pigment have been prepared; the results indicate that it contains two quinonoid carbonyl, two phenolic hydroxyl and two alcoholic hydroxyl groups. The infrared, ultraviolet and visible spectra of these derivatives suggest that cercosporin is a polyhydroxy derivative of a polycyclic quinone having an extended quinone structure in which two phenolic hydroxy groups are present in positions *peri* to the quinone carbonyls. Treating the pigment with conc. H_2SO_4 yields the purple noranhydrocercosporin $C_{28}H_{20}O_9$ which contains no methoxy groups. C.O.C.

Syntheses in the Carotenoid Series. IX—A New Synthesis of Symmetrical Carotenoids

O. Isler, M. Montavon, R. Rüegg, and P. Zeller

Ann., **603**, 129–144 (1957): *Chem. Abs.*, **51**, 14626 (10 Oct. 1957)

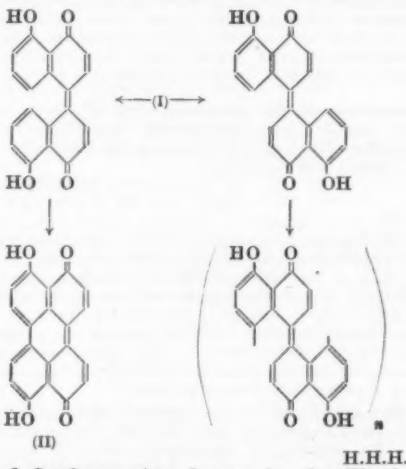
All-*trans*-β-carotene and a number of its derivatives have been prepared by a synthesis involving the new principle: $C_{14}+C_{12}+C_{14} = C_{40}$, in which C_{14} acetals react with a suitable sym. C_{12} dienol ether. C.O.C.

New Type of Melanin, and the Biogenesis of a Perylene Derivative

J. D. Bu'Lock and D. C. Allport

Proc. Chem. Soc., 264 (Sept. 1957)

The principal constituent of ether extracts of the fruit-bodies of *Daldinia concentrica* is established as the easily autoxidised polyphenol 4:5:4′:5′-tetrahydroxy-1:1′-dinaphthyl (I), which is readily converted into 4:9-dihydroxy perylene-3:10-quinone (II) by conc. HNO_3 or by chloranil. Most of the black pigment of the fruit-bodies, however, appears to be quite insol., polymeric, and firmly bound to the cell-wall material, and both II and the pigment are most probably formed *in situ* from the dinaphthyl I by intra- and inter-molecular variants of the oxidative coupling reaction, analogous to the cyclisation of protohypericin (cf. Brockmann, *Angew. Chem.*, 706 (1955)). The pigment is provisionally characterised as a quinonoid polymer (III) formed *in vivo* by oxidative condensation of a phenolic precursor, and appears to be a novel type of melanin derived from a naphthalene precursor.



(II)

H.H.H.

Effect of Surface-active Agents in the Physico-technical Preparation of Lithopone (C.I. Pigment White 5)

N. S. Rassudova

Trudy Moskov. Khim.-tekhnol. Inst., (18), 179–184 (1954): *Referativ. zhur. khim.*, 2353 (1956): *Chem. Abs.*, **51**, 18640 (25 Nov. 1957)

Lithopone (ZnS, $BaSO_4$) was produced at dilution 1:7 by using 1·5–7·0% of Petrov catalyst and *iso*butyl naphthalenesulphonate. Different amounts of the wetting agent and/or catalyst speeded or retarded precipitation resulting in products of different degrees of dispersion and properties. Precipitation was quickest when 3% of the catalyst was used. Increasing the dilution to 1:12 and 1:40, the catalyst having been added to the BaS solution, considerably speeds up settling. Addition of the wetting agent increased the intensity of the lithopone by 15–30%, hiding power by 30%, decreased the oil absorption by 25% and improved the pigment's grinding properties. C.O.C.

Oxidation of Litharge in a Fluidised Layer

N. A. Zozulin and N. V. Ogarev

Khim. prom., 149–153 (1957): *Chem. Abs.*, **51**, 18640 (25 Nov. 1957)

When forming red lead (C.I. Pigment Red 105) from litharge (C.I. Pigment Yellow 46) having the material as a fluidised bed was found practicable in the laboratory and gave indications of the great advantages likely to be

obtained in an automatic process, starting with the oxidation of lead and eliminating storage and cooling of PbO. The reaction can be speeded up by the use of oxygen, contamination of the product with iron oxides can be completely eliminated, and a more uniform product can be obtained. In a laboratory plant a quartz reactor was used, the time for PbO oxidation at 420–428°c. was found to be $\tau_1/\tau_2 = (p_2/p_1)^{\frac{1}{3}}$ (p_2 and p_1 = partial pressures of O_2; τ_1 and τ_2 = reaction time). The particles of PbO tended strongly to agglomerate, but this was overcome by mechanically applied sonic vibrations. The optimum gas velocity in the reaction was 0·04 m./sec., and the pressure needed to maintain the fluidised state was $p = (H-\varepsilon)v$ (H = height of layer at rest; ε = porosity of the material; v = sp.wt. of the material in kg./cu.in.). C.O.C.

Preparation of Ferric Red by a Topochemical Method
A. Krause and M. Kranz
Przemysl Chem., (6), 312–315 (1956): *Polish Tech. Abs.*, (25), 79 and 81 (1957)

Elaboration of a new simple method of preparing a yellow precipitate of basic ferric sulphate from ferric sulphate $Fe(SO_4)_3.9H_2O$ by treating with dilute NaOH. The yellow precipitate of ferric iso-ortho-hydroxide sulphate thus obtained was dehydrated by topochemical treatment in sodium hydroxide in an autoclave at high temperature and pressure. A series of red and pink ferric pigments with suitable technical properties was prepared. The influence of parameters, including NaOH concn., temperature, pressure, and the time of heating was investigated, and the optimum conditions were determined for preparing valuable ferric pigments of bright colours. The high rate at which nuclei formed favoured the obtaining of a red preparation of α-Fe_2O_3, containing an admixture of yellow α-FeOOH. The method described can be used on the technical scale. C.J.W.H.

Red Pigments composed of Ferric Oxide and of Sulphates of Alkaline-earth Metals in the Systems Fe_2O_3–$BaSO_4$, Fe_2O_3–$SrSO_4$, and Fe_2O_3–$CaSO_4$
M. Kranz
Przemysl Chem., **13**, 171–177 (1957): *Chem. Abs.*, **51**, 15143 (10 Oct. 1957)

Red pigments were prepared according to the reaction $Fe_2(SO_4)_3 + 3M(OH)_2 = 2Fe(OH)_3 + 3MSO_4$ (M = Ba, Sr or Ca). They were similarly prepared by using chlorides instead of the hydroxides and precipitating the metal ions with a solution of NaOH and Na_2SO_4. Isolating the Fe as basic sulphate gives better pigments than isolating it as ferric hydroxide. The influence of the experimental condition on the colour and quality of the pigments is discussed. C.O.C.

Chromium Titanate— a Green Pigment
N. S. Rassudova and G. A. Litvyak
Trudy Moskov. Khim.-tekhnol. Inst. im. D.I. Mendeleeva (22), 227–231 (1956): *Chem. Abs.*, **51**, 16173 (10 Nov. 1957)

Green pigments based on $Cr_2O_3.3TiO_2$ (from H_2TiO_3 and $Na_2Cr_2O_7.2H_2O$) have high fastness to light and heat. They are particularly inert to acids and bases and have anticorrosive properties. X-Ray studies confirm that $Cr_2O_3.3TiO_2$ is a chemical compound. C.O.C.

PATENTS

β-Carotene
F. Hoffmann–La Roche & Co. *BP* 787,497

β-Carotene, C.I. 75130, can be synthesised without use of hydroxylic intermediates by using a $C_{10}+C_{20}+C_{10} = C_{40}$ scheme. Thus 2:6:11:15-tetramethylhexadecahexaen-(2:4:6:10:12:14)-ine-(8)-dial-(1:16) is condensed with β-*cyclo*geranylene-triphenylphosphine and then the triple bond of the resulting compound is catalytically partially hydrogenated and isomerised in a known manner. The product is used as a food dye. C.O.C.

Dehydro-β-Carotene
F. Hoffmann–La Roche & Co. *BP* 786,003

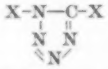
3,4;3′,4′;15,15′-Trisdehydro-β-carotene and 15,15′-monocis-3,4;3′,4′-bisdehydro-β-carotene are readily converted into all-trans 3,4;3′,4′-bisdehydrocarotene which is used for colouring butter, margarine, and cheese. They are obtained by condensing acetylene with 8-[2′,6′,6′-trimethyl*cyclo*hexadien-(1′,3′)-yl-(1′)]-2,6-dimethyloctatrien-(2,4,6)-al-(1) or 8-[2′,6′,6′-trimethyl*cyclo*hexen-(2′)-ylidene-(1′)]-2,6-dimethyloctatrien-(2,4,6)-al-(1) in a metal-organic reaction. The resulting 1,18-di-[2′,6′,6′-trimethyl*cyclo*hexadien-(1′,3′)-yl-(1′)]-3,7,12,16-tetramethyl-8,11-dihydroxyoctadecahexaen-(2,4,6,12,14,16)-ine-(9) or 1,18-di-[2′,6′,6′-trimethyl*cyclo*hexen-(2′)-ylidene-(1′)]-3,7,12,16-tetramethyl-8,11-dihydroxyoctadecahexaen-(2,4,6,12,14,16)-in-(9) is subjected to bilateral alkyl rearrangement and dehydration, and, if desired, the 3,4;3′,4′;15,15′-trisdehydro-β-carotene partially hydrogenated at the triple bond to yield 15,15′-monocis 3,4;3′,4′-bisdehydro-β-carotene. This is in turn converted into all-trans 3,4;3′,4′-bisdehydro-β-carotene by isomerisation. C.O.C.

Carotenoid Compounds— Food Dyes
F. Hoffmann–La Roche & Co. *BP* 788,266

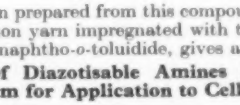
3:4;15:15′-bisdehydro-β-carotene and 15:15′-monocis 3:4-dehydro-β-carotene are prepared by condensing acetylene through one of its reactive H atoms with 8-[2′:6′:6′-trimethyl*cyclo*hexadiene-(1′:3′)-yl-(1′)]-2:6-dimethyloctatrien-(2:4:6)-al-(1) and through other of its reactive H atoms with 8-[2′:6′:6′-trimethyl*cyclo*hexen-(1′)-yl-(1′)]-2:6-dimethyloctatrien-(2:4:6)-al-(1) by a metal-organic reaction. The 1-[2′:6′:6′-trimethyl*cyclo*hexadien-(1′:3′)-yl-(1′)-18-[2′:6′:6′-trimethyl-*cyclo*hexen-(1′)-yl-(1′)]-3:7:12:16-tetramethyl-8:11-dihydroxyoctadecahexaen-(2:4:6:12:14:16)-ine-(9) so produced is subjected to bilateral alkyl rearrangement and dehydration. This yields 3:4,15:15′-bisdehydro-β-carotene which can be partially hydrogenated at the triple bond to give 15:15′-monocis 3:4-dehydro-β-carotene which in turn can be converted into all-trans 3:4-dehydro-β-carotene by isomerisation. They are used as food dyes. C.O.C.

Aminophenyltetrazoles— Diazo Components for Azoic Dyes and Pigments
FH *BP* 787,582

Aminophenyltetrazoles



(one X = aminophenyl which may carry substituents; the other X = Alk, Ar, Aralk, or cycloalkyl) give azoic dyes of good fastness to peroxide when diazotised and coupled on the fibre with arylides of 3:2-hydroxynaphthoic acid and other coupling components generally used for this type of work. Thus *N*-aceto-3-nitro-4-ethoxyanilide is converted into its imide-chloride which is reacted with hydrazoic acid to give the tetrazole. Reduction then gives the amino compound



A diazo solution prepared from this compound, when used to develop cotton yarn impregnated with the sodium salt of 3:2-hydroxynaphtho-*o*-toluidide, gives a red. E.S.

Production of Diazotisable Amines in a Finely-dispersed Form for Application to Cellulose Acetate and Nylon
General Aniline *USP* 2,734,793

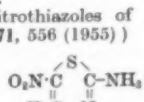
Diazotisable amines of low aq. solubility such as *p*-nitro-*o*-anisidine are wet-ground with sodium lignosulphonate or secondary liquorice extract to give fine dispersions suitable for application to cellulose acetate and nylon along with suitable coupling components for the production of azoic dyeings and prints. E.S.

Azo Couplings at Relatively High Temperatures
General Aniline *USP* 2,746,955

Some azo couplings, particularly those with urea di-J acid, proceed more smoothly, and give a product which filters more readily, if the solution of the coupling component is maintained at 40–55°c. whilst running in the diazo solution. E.S.

Monoazo Disperse Dyes from 2-Amino-5-Nitrothiazoles
Eastman Kodak Co. *USP* 2,746,953

The 2-amino-5-nitrothiazoles of *USPs* 2,683,708 and 2,683,709 (J.S.D.C., **71**, 556 (1955)))

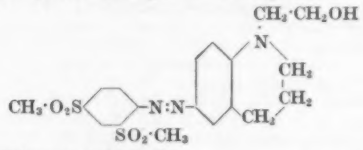


(X = H, Alk of 1–6 C, CN, CF_3, phenyl, or subst. phenyl) are diazotised and coupled with primary monoamines of the benzene series to give red, violet, and blue disperse dyes, whose primary amino groups may be diazotised on the fibre and coupled with suitable developers to give dark shades. Thus the monoazo compound 2-amino-5-nitrothiazole→2:5-dimethoxyaniline dyes cellulose acetate reddish violet, and may be diazotised on the fibre and coupled with 3:2-hydroxynaphthoic acid to give black. E.S.

Monoazo Disperse Dyes from 2:4-Bis(methylsulphonyl)aniline

Eastman Kodak Co. *USP* 2,746,952

2:4-Bis(methylsulphonyl)aniline is diazotised and coupled with tetrahydroquinoline and its derivatives to give rubine and violet disperse dyes. Thus, using *N*-β-hydroxyethyltetrahydroquinoline, the product

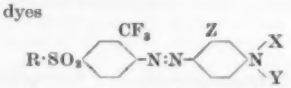


dyes cellulose acetate rubine. E.S.

Orange and Red Monoazo Disperse Dyes

ICI *BP* 789,025

Disperse dyes



(R = Alk of 1–4 C; X = β-hydroxyethyl, γ-hydroxypropyl, or β:γ-dihydroxypropyl; Y = Alk of 1–4 C, β-hydroxyethyl, or γ-hydroxypropyl; Z = H, Hal, CH_3, or CF_3) dye nylon as well as cellulose acetate bright orange and red. Thus the monoazo compound 2-amino-5-ethanesulphonylbenzotrifluoride→*N*:*N*-bis-β-hydroxyethyl-*m*-toluidine dyes cellulose acetate bright reddish orange and nylon bright scarlet. E.S.

Glucoside Azo Dyes

Research Corpn. (New York) *USP* 2,748,107

The glucosides naringin and hesperidin obtained from citrus fruit are coupled with diazotised arylamines to give azo compounds which are acid and chrome dyes and may be used as wood stains. Thus aniline (9·3 parts) is diazotised and coupled with naringin (58 parts) in presence of alkali. The product dyes wool from an acid bath yellow to orange, converted to olive green by afterchroming. E.S.

Red Monoazo Pigments

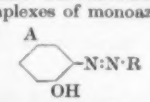
DuP *USP* 2,744,027

The insoluble metal lakes of the monoazo compound 4-amino-2-chloroanisole-5-sulphonic acid→3:2-hydroxynaphthoic acid are weak and dull, but if it is mixed with the monoazo compound 4-amino-2-chlorotoluene-5-sulphonic acid→3:2-hydroxynaphthoic acid before laking, strong bluish red pigments are obtained. Mixtures containing 75–85% of the toluene analogue and 25–15% of the anisole analogue give the best results, and the mixtures are conveniently made by mixing the diazo components before diazotising and coupling with 3:2-hydroxynaphthoic acid. E.S.

Metal(Chromium)-complex Monoazo Dyes of Improved Wet-fastness on Wool and Nylon

FH *BP* 787,986

Chromium complexes of monoazo dyes free from nuclear SO_3H groups, and containing the group $-SO_2\cdot CH_2\cdot CH_2\cdot O\cdot SO_3H$ (I) or $-SO_2\cdot CH{:}CH_2$ (II) have very good wet-fastness, as II, either formed during the dyeing process or already present, combines with wool keratin. The preferred dyes are 1:2 Cr-dye complexes of monoazo compounds



(A = I or II; R = residue of a naphthol or keto-enol compound). Thus 2-amino-4-β-hydroxyethylsulphonylphenol is diazotised and coupled with 3-methyl-1-phenyl-5-pyrazolone, and the dried monoazo compound is sulphated by stirring with 96% H_2SO_4. Boiling with aq. sodium chromosalicylate gives the complex, which dyes wool orange red from a neutral or weakly acid bath. E.S.

Metal(Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc.

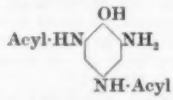
Ciba *BP* 789,002

The complexes containing 1 atom of Co, 1 mol. of a monoazo compound *o*-aminophenol→*o*-coupling primary naphthylamine, and 1 mol. of a monoazo compound *o*-aminophenol-sulphonamide or -sulphone→*o*-coupling hydroxy-compound, both monoazo compounds being free from SO_3H and COOH groups, dye wool, etc. from neutral or weakly acid baths. β-Naphthylamine is the preferred *o*-coupling primary amine, but 2-naphthylamine-1-sulphonic acid may be used, the SO_3H group being split off in coupling. Thus 1 mol. of each of the monoazo compounds 2-amino-5-nitrophenol→β-naphthylamine and 2-aminophenol-4-sulphonmethylamide→*N*-acetoacet-*o*-chloroanilide dissolved in aq. NaOH are stirred at 80–85°C. with $CoSO_4$ to give the complex which dyes wool green. E.S.

Metallisable Monoazo Wool Dyes from 2-Amino-4:6-Bisacylaminophenols

FBy *BP* 789,126

2-Amino-4:6-bisacylaminophenols



(Acyl = e.g. acetyl, chloroacetyl, methanesulphonyl) are diazotised and coupled with *o*-coupling naphthols, pyrazolones, or acetoaceticanilides to give monoazo dyes which may be metallised in substance, on the fibre, or in the dyebath. Thus, 2-amino-4:6-bisacetylaminophenol is diazotised and coupled with β-naphthol in presence of NaOH and Na_2CO_3. The product dyes wool dark blue by the metachrome process. E.S.

Red Metallisable and Metal-complex Monoazo Pyrazolone Dyes for Wool, Nylon, etc.

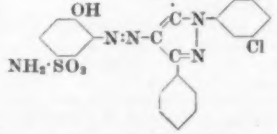
S *BP* 787,843

1-Cyanophenyl-5-pyrazolones, when coupled with the diazo compounds of *o*-aminophenols having an alkylsulphonyl or sulphonamide substituent, give monoazo dyes whose Co and Cr complexes are red, the cyano group exerting a marked bathochromic effect. Thus the monoazo compound 2-aminophenol-4-sulphonanilide→1-*p*-cyanophenyl-5-pyrazolone-3-carboxamide is a red metachrome dye. E.S.

Metal(Chromium and Cobalt)-complex Monoazo Pyrazolone Dyes for Wool, Nylon, etc.

Ciba *BP* 788,157

Sulphonamides of *o*-aminophenols are diazotised and coupled with 3-phenyl- and 1:3-diphenyl-5-pyrazolones and the products converted into 1:2 metal complexes with Cr and Co to give neutral-dyeing wool dyes similar to those of *BP* 741,602 (J.S.D.C., **72**, 65 (1956)), in which 3-methyl-1-phenyl-5-pyrazolones are used as coupling components. Thus 2-aminophenol-4-sulphonamide is diazotised and coupled with 1-(5′-chloro-2′-methylphenyl)-3-phenyl-5-pyrazolone in presence of Na_2CO_3, and the product

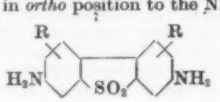


boiled with aq. sodium chromosalicylate to give the Cr complex which dyes wool red-orange. E.S.

Blue, Metallisable Disazo Direct Dyes from Substituted Benzidine Sulphones

American Cyanamid Corpn. *USP* 2,752,333

Tetrazotised benzidine sulphones having chelating substituents (R) in *ortho* position to the NH_2 groups—

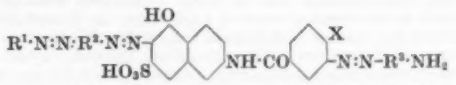


are coupled with *ortho*-coupling naphtholsulphonic acids, etc., to give greenish blue direct dyes which may be metallised (esp. coppered) in substance or on the fibre. Thus dianisidine is diacetylated and heated at 60°c. in 35% oleum, followed by hydrolysis to give the sulphone monosulphonic acid. Refluxing with 50% H_2SO_4 then gives the sulphone of hydroxymethoxybenzidine, which on acetylation, methylation, and hydrolysis yields the dimethoxybenzidine sulphone (R = OCH_3). This is tetrazotised and coupled with 2 mol. of 1-amino-8-naphthol-2:4-disulphonic acid in presence of pyridine. The product dyes cotton greenish blue, or it may be heated with ammoniacal $CuSO_4$ to give the metal-complex. E.S.

Red and Violet Trisazo Direct Dyes for Diazotisation and Development on the Fibre

DuP *USP* 2,750,376

Trisazo dyes



(R^1 = residue of benzenemonosulphonic acid or naphthalenedisulphonic acid; R^2 = benzene residue which may carry substituents such as Hal, CH_3, OCH_3, etc.; the 2 azo links in R^2 being *para* to each other; $R^3{\cdot}NH_2$ = aniline or its Hal, etc. derivatives or α-naphthylamine and its sulphonic acids; X = H or CH_3). Thus 4-aminoazobenzene-4′-sulphonic acid is diazotised and alkali-coupled with *m*-aminobenzoyl-J acid. The aminodisazo compound so formed is then diazotised and coupled with *N*-methylaniline-ω-sulphonic acid in presence of sodium acetate. Hydrolysis with aq. NaOH then removes the methylsulphonic acid group, giving the aminotrisazo compound, which gives dischargeable red on cotton when diazotised on the fibre and developed with β-naphthol. E.S.

Azoic Compositions

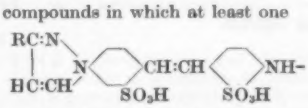
FBy *BP* 788,689

Combinations of diazotised weakly negative substituted amines of the benzene series containing a benzoylamino group *p*- to the diazotised amino group and which are substituted also by alkyl or alkoxy groups or by halogenations (but no alkoxy group *o*- to the diazotised amino group) with 2-alkylamino-5(4)-sulphobenzoic acids are readily developed by neutral steaming, e.g. diazotised 1-amino-3-chloro-4-benzoylamino-6-methylbenzene is heated with 2-methylamino-5-sulphobenzoic acid to yield the diazoamino compound. This is made into a printing paste with 1-(2′:3′-hydroxynaphthoylamino)-2-methyl-4-methoxybenzene. On application and neutral steaming a bordeaux print very fast to light and reduction discharging is obtained. C.O.C.

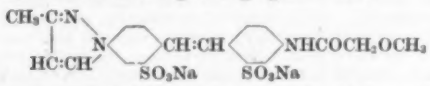
Fluorescent Brightening Agents

FBy *BP* 787,429

Stilbene compounds in which at least one



(R = hydrocarbon) group is attached to certain radicals, e.g. mono- or poly-basic carboxylic acid radicals, are excellent fluorescent brightening agents. Thus

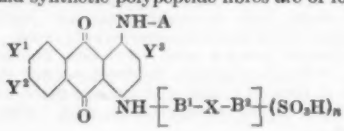


is a fluorescent brightening agent applicable to cellulose from alkaline synthetic detergent liquors. C.O.C.

Anthraquinone (Acid) Dyes

Gy *BP* 787,371

Reddish- to greenish-blue dyes dyeing wool from neutral or weakly acid baths and also suitable for dyeing other natural and synthetic polypeptide fibres are of formula—



(A = a *cyclo*hexyl radical; B^1 = a phenylene radical B^2 = an aryl radical; X = O or S; Y^1, Y^2, Y^3 = H or Hal; *n* = 1 or 2). They are prepared by reacting a 1-*cyclo*hexylamino anthraquinone having a replaceable group in the 4-position, e.g. Br, with an aminophenylarylether, separating and sulphonating. Thus, 1-(4′-*cyclo*hexyl-*cyclo*hexylamino)-4-bromoanthraquinone (46·6) is stirred for 24 hr. at 110–115°c. in *n*-butyl alcohol (50) with 2-amino-5-chlorodiphenylether (38·5), K acetate (10·4), and Cu acetate (1·0). *n*-Butyl alcohol (100) is added at 100°c., and the whole stirred for 3 hr. at 80–90°c. after which the product is filtered, washed, and dried. The base is then sulphonated with conc. H_2SO_4, oleum or chlorosulphonic acid and separated as the alkali metal salt. The products have good fastness to milling and light. E.T.

Anthraquinone Dyes

BASF *BP* 787,716

Anthraquinone compounds which dye wool, silk, polyamide, polyurethane, and regenerated casein fibres from neutral or weakly acid dispersions are produced by reacting anthraquinone dyes with at least one organic N-containing base. The anthraquinone dyes used consist of two 1-amino-4-arylaminoanthraquinone-2-sulphonic acid radicals linked to each other at the *para*-C atoms of the aryl group either directly or via a bridge member. The anthraquinone nuclei of the initial dye may be substituted in the 5-, 6-, 7-, and/or 8-positions with, e.g. Hal or acylamino; the substitution may be symmetrical or unsymmetrical. The aryl groups linking the 4-positions may also be substituted with Alk or OAlk. The bridge member between the aryl groups may be –O–, –S–, –SO–, $–SO_2–$, –CO–, –NH– or a subst. or unsubst. alkylene group. Such dyes may be prepared by condensing 1-amino-4-bromoanthraquinone-2-sulphonic acids with diamines by the method of *USP* 2,156,887. Suitable organic N-containing bases are compounds containing aliphatic, hydroaromatic, araliphatic or aromatic amino- and/or imino groups, e.g. di*cyclo*hexylamine, benzylamine, aniline, quinoline. Reaction occurs when the initial soluble dye and the organic base are heated in aq. or aq. alcoholic media and the products are insoluble or slightly soluble but show better fastness properties and greater clarity of shade than the initial dyes. E.T.

Anthraquinone Vat Dyes

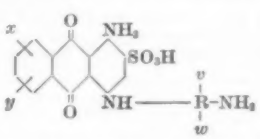
FBy *BP* 788,433

Olive-green dyes for cotton, of excellent fastness, are produced by introducing substituted sulphonamide groups into the molecules of vat dyes made by the method of *BP* 773,116 (J.S.D.C., **73**, 405 (1957)). Thus, 6·7 pts. of the vat dye of Example 1 (*BP* 773,116) are dissolved in chlorosulphonic acid (35 ml.) at 20–30°c.; the melt is poured on to ice when reaction is complete, filtered and washed neutral. The moist cake is then stirred with 30% dimethylamine solution (100 ml.) at room temperature for some hours, heated at 80°c. and finally to the boil, giving the sulphodimethylamide in good yield after filtering and washing. Other amines, e.g. monomethylamine or aniline, and cyclic N-containing bases, e.g. morpholine, piperidine or 1:2:3:4-tetrahydroquinoline, may be used. The products give greener dyeings than the starting materials, e.g. olive-green instead of khaki, and have superior wet fastness to the similarly constituted vat dyes made by the method of *GP* 655,591. E.T.

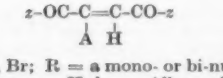
Substantive Anthraquinone Dyes

Saul & Co. *USP* 2,779,772

Green dyes for cotton or regenerated cellulose having very good light fastness, good wet fastness, and good solubility and exhaustion properties are made by condensing, in mol. proportions which differ from each other by $\lesssim$ 10%, a 1-amino-anthraquinone-2-sulphonic acid of formula—



and a similar 1-amino-anthraquinone-2-sulphonic acid of different formula by treatment with a dicarboxylic acid halide—



(A = H, CH_3, Cl, Br; R = a mono- or bi-nuclear radical of the benzene series; v = H, lower Alk or alkoxy or SO_3H; w = H, lower Alk or alkoxy; x = H, Cl, Br or SO_3H; y = H or Cl; z = Cl or Br). The wet fastness and the solubility of these dyes are better than those of the similar dyes made by the method of *USP* 2,623,884.

E.T.

Quinizarin

General Aniline *USP* 2,752,364

A high-boiling solvent, preferably trichlorobenzene, is added to the usual reaction melt containing *p*-chlorophenol, phthalic anhydride, boric acid and sulphuric acid. The melt, heated at 200°C., normally gives off large amounts of HCl gas which carry phthalic anhydride as vapour into the vessel outlets where it condenses and forms blockages. Addition of the solvent in sufficient quantity to form a surface film prevents this and also eliminates surface foaming of the melt. E.T.

Indanthrone Vat Dyes

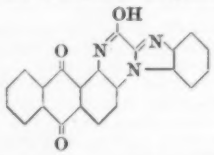
Ciba *BP* 787,908

Indanthrone vat dyes are produced more economically by fusion of 1-aminoanthraquinones with alkali metal phenolates in melts which contain much smaller proportions of the phenolates than those used in similar earlier methods, viz. *BP* 5959/1906 and *BP* 703,377 (J.S.D.C., **70**, 203 (1954)). Difficulties in stirring the melts which tend to arise when using the smaller quantity of phenolate are overcome (*a*) by having a 4–5% excess of the phenol over the KOH or NaOH used to form the phenolate, and (*b*) by maintaining a high partial pressure of water vapour above the melt. Oxidising agents, e.g. K or Na nitrates, persulphates, perborates or chlorates or MnO_2 and/or Fe_2O_3, are added to the melts as aq. solutions or dispersions. Heating is carried out so that water distils slowly, but sufficient to maintain fluidity is always retained. The apparatus used is such that water can be injected into the melt if necessary to maintain fluidity. Besides phenol, *o*-, *m*- or *p*-cresols can be used. E.T.

Quinoxaline Vat Dyes

DuP *USP* 2,751,385

Scarlet and yellow vat dyes of the quinoxaline series, e.g.

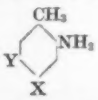


(14 - hydroxybenzimidazo - [1:2-*a*]naphtho - [2:3-*f*] - quinoxaline-7:12-dione) having good light fastness are produced by heating 2:3-dihydroxynaphtho[2:3-*f*]quinoxaline-7:12-dione (3) with anthranilic acid (11), boric acid (3), and phenol (30) at 160–70°C. for 6 hr. The mixture is cooled, filtered and washed with ethanol to give dark red crystals (2) of m.p. 340°C. which dye cotton scarlet. Alternatively, 1:2-diaminoanthraquinone (50), anhydrous oxalic acid (100) and phenol (250) are heated at 135–140°C. for 90 min.; then 30 min. under reflux. Anthranilic acid (60) and boric acid (15) are added at 150°C. and more anthranilic acid (60) is added after 6 hr. refluxing. Heating under reflux continues until reaction is complete. Other dyes of the series are produced by introducing 1 or 2 Cl or Br atoms into the nucleus or by methylating the OH group. E.T.

Perylene Vat Dyes

FBy *BP* 788,777

Bright yellowish-scarlet vat dyes of excellent fastness to ight, chlorine and washing are prepared by condensing perylene-3:4:9:10-tetracarboxylic acid or a functional derivative with aromatic amines of formula—



(X = Cl or Br; Y = H, Cl or Br). Condensation occurs (*a*) in solvents, e.g. nitrobenzene, glacial HAc, etc.; (*b*) in aq. solutions under pressure; or (*c*) in excess of the amine. Thus, perylene-3:4:9:10-tetracarboxylic acid anhydride (43) and 4-chloro-2-amino-1-methylbenzene (300) are heated at 140–150°C.; anhydrous $ZnCl_2$ (4) is added and the temperature is raised to 200–210°C. Condensation is complete after several hours and the melt is cooled to 100°C., ethyl alcohol (400) is added and the product filtered at 50–60°C., washed with alcohol and dried. The clear colours given by these dyes contrast with the bluer and much duller reds given by dyes produced by the method of *BP* 201,786 (J.S.D.C., **40**, 237 (1924)), in which NH_3, primary aliphatic or other aromatic amines were used.

E.T.

10-(1′ or 2′-Naphthoyl)-3:7-bis(dimethylamino)-phenothiazine and 10-(3- or 4-Nitrobenzoyl)-3:7-bis(dimethylamino)phenothiazine

National Cash Register Co. *BP* 788,384

The zinc chloride salt of leuco Methylene Blue (C.I. 52015) when treated with 1-naphthoyl or 2-naphthoyl chloride in pyridine and poured into water yields a precipitate. This when treated with alkali, filtered, extracted with benzene, this solution then treated with fuller's earth, filtered and the filtrate precipitated with petroleum ether, yields 10-(1′- or 2′-naphthoyl)-3:7-bis(dimethylamino)-phenothiazine. This compound is very stable to light, it is a very pale yellow but turns blue-green on prolonged contact with attapulgite or halloysite.

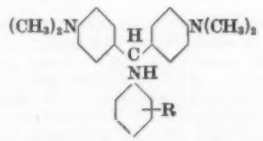
BP 788,390

10 - (3- or 4 - Nitrobenzoyl) - 3:7 - (dimethylamino) phenothiazine are similarly produced from leuco Methylene Blue and 3-nitro- or 4-nitrobenzoyl chloride. They are very fast to light and light orange yellow but become intensely blue-green on prolonged contact with attapulgite or halloysite. C.O.C.

Derivatives of leuco Auramine

National Cash Register Co. *BP* 788,427

Compounds of formula—



(R = *o*- or *p*- Cl or Br, 2:3-, 2:4-, 2:5-, 3:4- or 3:5-dichloro or bromo, 2:3:4-, 3:4:5-, 2:3:5-, or 2:4:5-trichloro or bromo, or 2:3:4:5-tetrachloro or bromo) are solid practically colourless materials of excellent fastness to light but which turn dark blue or dark blue-green also of excellent light fastness on adsorption in contact with acidic inorganic compounds, e.g. attapulgite, aluminium sulphate or zinc sulphide. C.O.C.

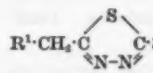
3 - Phenyl - 7 - ureidocoumarins as Fluorescent Brightening Agents

Gy *BP* 786,234

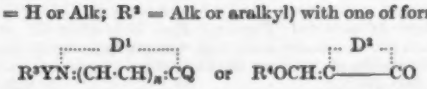
A benzaldehyde having in 2-position a hydroxyl group and in 4-position an acylamine or nitro group is condensed with an acetic acid derivative containing a phenyl, halogen or alkyl-subst. phenyl substituent at the α-C atom to form the corresponding β-phenylacrylic acid derivative. The OH group in the *o*-position to the acrylic acid radical is joined with the COOH of the acid radical to form the coumarin ring. At aq. stage of the reaction the acylamino group is saponified or the nitro group reduced and reacted with a carbamic acid derivative to form the ureido group. Thus 2-methoxy-4-acetyl amino benzaldehyde is condensed with benzylcyanide to yield α-phenyl-β-(2-methoxy-4-acetylaminophenyl)-acrylonitrile. This is then treated with anhydrous $AlCl_3$ in benzene, refluxed for 6 hr., cooled and iced HCl added. The yellow mixture obtained is treated with a mixture of acetic and hydrochloric acids and hydrolysed to yield the colourless 3-phenyl-7-amino coumarin. This is converted to the hydrochloride and treated with excess phosgene to yield 3-phenylcoumarinyl-(7)-*iso*-cyanate which with monoethanolamine yields *N*-(β-hydroxyethyl)*N*′-[3-phenylcoumarinyl-(7)]-urea. This is a pale yellowish powder with vivid blue fluorescence in daylight. It has good affinity for wool, acetate rayon and nylon. It is faster to light and gives a more blue-white shading than do the commercially used 7-alkyl amino coumarins. C.O.C.

Methin Cyanine and *mero*Cyanine Dyes
Ilford *BP* 785,939

Photographic dyes are obtained by condensing a compound of formula—



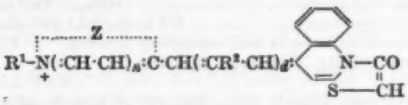
(R^1 = H or Alk; R^2 = Alk or aralkyl) with one of formula



(n = 0, 1 or 2; R^3 = Alk, aralkyl or hydroxyalkyl; Y = acid radical; D^1 = atoms to complete a heterocyclic ring; Q = a thio ether, thioethervinyl or acetanilidovinyl group; D^2 = atoms to complete a heterocyclic keto methylene ring; R^4 = Alk). Thus 2:3-dimethyl-5-methylthio-1:3:4-thiodiazolium iodide was treated with 2:2′-acetanilidovinylbenzo oxazole ethiodide in ethanol in presence of triethylamine to yield the bluish red dye (3-methyl-5-methylthio-2-1:3:4-thiadiazole)(3-ethyl-2-benzoxazole) trimethinecyanine iodide. C.O.C.

Un-ionised Cyanine Dyes
Eastman Kodak Co. *USP* 2,748,115

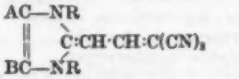
Dyes of formula—



(R^1 = Alk; R^2 = H, Alk or Ar; n and d = 0 or 1; Z = atoms to complete a 5- or 6-membered ring), e.g. anhydro-3-ethyl-1′-hydroxyoxa-5′(thiazolo[3,2-*a*]quino)-carbocyanine hydroxide, have photosensitising properties. C.O.C.

New Cyanine Dyes
ICI *BP* 786,169

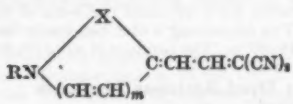
Dyes of formula—



(R = Alk; A and B = H or atoms to complete a benzene ring fused to the heterocyclic ring), e.g. the yellow dye obtained by condensing 2-β-acetanilidovinyl-1:3-dimethylbenzimidazolium iodide with malonic dinitrile methanol in presence of trimethylamine, have photographic sensitising properties.

BP 786,168

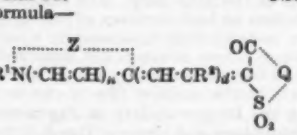
Dyes of formula—



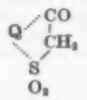
(m = 0 or 1; R = Alk or allyl; X = atoms to complete a 5- or 6-membered ring), e.g. 4-(1-ethyl)-1:2-dihydroquinolylidene-2-)-2-cyano-2-butenonitrile, or those described in *BP* 786,169 (above), when mixed with a compound of formula $(CN)_2$:CH·(CH:CH)$_n$·NHAr (n = 0, 1 or 2), e.g. *N*-(2:2-dicyanovinyl)-aniline, act as photographic supersensitisers. C.O.C.

***mero*Cyanine Dyes containing a Sulphone Group**
Eastman Kodak Co. *USP* 2,748,114

Dyes of formula—



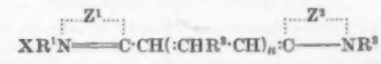
(R^1 = Alk; R^3 = H or Alk; m = 0 or 1; d = 0, 1 or 2; Q = atoms to complete a 5-membered ring; Z = atoms to complete a 5- or 6-membered ring), are prepared by treating a suitable cylammonium quaternary salt with a compound of formula—



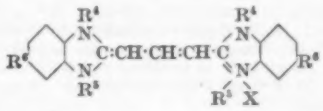
Thus, 5-[(3-ethyl-2(3*H*)-benzothiazolylidene)ethylidene]-3-methyl-2-phenyl-4-thiazolidone-1:1-dioxide is obtained by refluxing 3-methyl-2-phenyl-4-thiazolidene-1:1-dioxide with 2-β-acetanilidovinyl-3-ethylbenzoxazolium iodide in ethylalcohol using triethylamine as catalyst. C.O.C.

Benzimidazolocyanine Dyes
Eastman Kodak Co. *USP* 2,751,298

Dyes of formula—



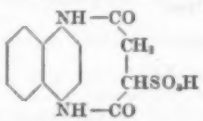
(R^1 and R^2 = Alk; R^3 = Alk, Ar or a pyrryl group; n = 0 or 1; X = anion; Z^1 and Z^2 = atoms to complete a 5- or 6-membered ring), e.g. 1′-ethyl-3-methylthia-2′-cyanine iodide used in conjunction with dyes of formula—



(R^4 and R^5 = Alk; R^6 = Br, acetyl or ethyl carbamyl), e.g. 5:5′-diacetyl-1:1′:3:3′-tetramethylbenzimidazolo-carbocyanine iodide, are photographic supersensitisers. C.O.C.

Oxidation Bases for Printing
Acna *BP* 787,357

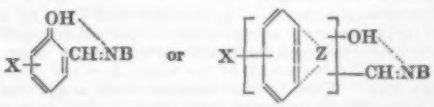
Oxidation bases yielding browns and blacks and which are more stable in storage than those formerly used are condensation products of subst. or unsubst. primary or secondary, aromatic or aliphatic-aromatic *mono-* or *poly*-amines, e.g. aniline, toluidine, chloro- or nitro-aniline, naphthylene diamine, ethylaniline, with *poly*basic organic acids, e.g. oxalic, succinic, tartaric, phthalic, sulphophthalic, carbonic or phosphoric acid. They must contain both amide groups and free acidic groups capable of rendering the products soluble in the form of salts; e.g. 1:4-naphthalenediaminesulphosuccindiamide



They are printed on all types of fibres, the paste being made up of the oxidation base, an oxidising agent, e.g. chromate, dichromate, chlorate or peroxide; a catalyst, e.g. Cu, Va, or Fe salt; polyglycol, water, and a substance capable of liberating acid on steaming. Steaming at moderate temperature gives browns or blacks of good general fastness. E.T.

Yellow Nonfluorescent Schiff's Bases
General Aniline *USP* 2,750,291

Compounds of formula—

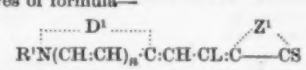


(X = H, Alk, hydroxyalkyl, Ar, NO_2, OH, SO_3H, COOH, acylamino, alkylamino, cyano or acyloxyalkyl; Z = atoms to complete a 6-membered aromatic or heterocyclic ring containing a conjugated unsaturated system; B = naphthyl) are yellow nonfluorescent dyes obtained by condensing an aromatic *o*-hydroxyaldehyde with a 1-naphthylamine substituent in position 8 by Hal, alkoxy, Alk, sulpho, carboxy, nitro or cyano. Thus potassium-5-formyl-6-hydroxynaphthalene-2-sulphonate (1 mol.) in a

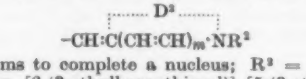
minimum quantity of boiling acetic acid is mixed with pyridine (3 mol.) and 1-aminonaphthalene-8-sulphuric acid (slightly less than 1 mol.), boiled for 3-5 min. and poured into excess ether to precipitate the dye. These yellow dyes are especially suitable for use as dischargeable filter dyes in the process described in *USP* 2,687,353. C.O.C.

Methin Dyes
Gevaert Photo-Producten *BP* 788,901

When phosphorus pentasulphide reacts in basic or neutral medium upon a merocyanine dye, the keto group of the dye adjacent to the C atom linked to the methin chain is converted into a thioketo group even when other keto groups are already present in the ketomethylene nucleus of the merocyanine. This principle is utilised to produce dyes of formula—



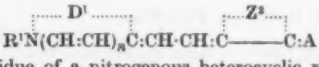
(D_1 = atoms to complete a nucleus; R^1 = Alk; Z^1 = atoms to complete the residue of a heterocyclic nucleus containing a thioketo group adjacent to the C atom linked to the methin chain; n = 0 or 1; L = H, Alk, Ar, S-alkyl or



(D^2 = atoms to complete a nucleus; R^2 = Alk; m = 0 or 1)), e.g. [2-(3-ethylbenzothiazol)] [5-(3-ethylthiazolidine-2:4-dione]-dimethin merocyanine heated with phosphorus pentasulphide in pyridine yields [2-(3-ethylbenzothiazol)] [5-(3-ethyl-4-thiothiazolidine dione]-dimethin merocyanine.

BP 789,077

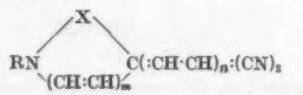
Dyes of the above formula are quaternised and then converted into polymethin and merocyanine dyes of formula—



(Z^2 = residue of a nitrogenous heterocyclic ring; A = $:CH\cdot C(:CH\cdot CH)_a:NR^3]X^-$ (a = 0 or 1; R^3 = Alk; X = anion) or :CPQ ($\overset{+}{P}$ + Q = NC– or together = atoms to complete a heterocyclic ketomethylene ring)). Thus [2-(3-ethylbenzthiazol)] [5 - (3 - ethyl -4 - thiothiazolidine-dione)] dimethin merocyanine is heated under pressure with methyliodide and methylalcohol to yield the dye [2 - (3 - ethylbenzothiazol)] [5 - (3 - ethyl - 4 - methyl-mercaptothiazoline-2-one)] dimethin merocyanine iodide. C.O.C.

***mero*Cyanine Dyes**
ICI *BP* 789,136

Dyes of formula—



(m = 0 or 1; n = 2 or 3; R = alkyl or Alk of < 6 C; X = atoms to complete a 5- or 6-membered ring which may form part of a condensed ring system), e.g. 6-(3′-ethyl-2′:3′-dihydrobenzthiazolylidene-2′)-2-cyano-2:4-hexadienonitrile, are powerful photographic sensitisers in the green and red regions of the spectrum. C.O.C.

Isolating the Colouring Compounds from Caramelised Sugar (C.I. Natural Brown 10)
Union Starch & Refining Co. *BP* 785,299

The caramel colour bodies are separated from an acid-proof type caramel colour syrup. The uncaramellised sugars are recovered and recaramellised so that the impurity and ash content of the sugar does not exceed a certain level. When the ash content of the sugar reaches that value which prevents formation of good acid-proof colourbodies, the ash may be removed, e.g. by ion exchange methods, or the syrup can be used to produce a different type of caramel colour. C.O.C.

Carbon Black (C.I. Pigment Black 7)
United Carbon Co. Inc. (Maryland) *BP* 786,730

A quick process for obtaining high yields of furnace black using furnaces larger than those hitherto used. C.O.C.

Carbon Black from Acetylene or Mixtures of Acetylene and Hydrocarbons
Knapsack-Griesheim *BP* 788,154

A greatly simplified process for obtaining pigment of desired bulk density. C.O.C.

Compositions containing Lead Chromate for Colouring Plastics
ICI *BP* 786,158

Addition of 5–75% by wt. on the lead chromate to pigments containing lead chromate, e.g. C.I. Pigment Yellow 34 and C.I. Pigment Red 104, of a di- or tri-carboxylic aromatic acid, e.g. terephthalic acid, renders them stable in plastics at high moulding temperatures, e.g. 260–280°c. C.O.C.

Lead Chrome Pigments for Colouring Cellulose Acetate
ICI *BP* 786,159

Lead chrome pigments, e.g. C.I. Pigment Yellow 34 and C.I. Pigment Red 104, are stable in cellulose acetate at 180–220°c. if 50–500% on the weight of the pigment of basic aluminium sulphate is incorporated in the pigment. C.O.C.

Silicic Acid and Pigments Containing it
FBy *BP* 786,754

Pigments of high brightening power, particularly for paper, are obtained by double decomposition of solutions of an alkaline earth metal chloride and an alkali metal silicate. The solutions are mixed so that the shearing force set up has a velocity gradient of < 100/sec. The strength of the solutions should be < 0·2 molar but yet such that the reaction mass is still capable of flowing. C.O.C.

Organophilic Titanium Dioxide
DuP *USP* 2,749,248

Titanium dioxide (C.I. Pigment White 6) of particle size < 1 mm. is finely ground in presence of an ethylenic compound capable of undergoing addition polymerisation, e.g. styrene. C.O.C.

Zinc Oxide, C.I. Pigment White
American Zinc, Lead & Smelting Co. *USP* 2,747,966

Production of American process zinc oxide by keeping the granules of zinciferous materials in a fluidised condition during their heating and reduction. The heating and reduction are automatically alternated. Only a gaseous reducing agent, e.g. methane, is used. C.O.C.

Flushing Pigments or the Like
Dehydag Deutsche Hydrierwerke *BP* 786,312

*cyclo*Hexylamines alkylated in the nucleus or their soaps with resin or fatty acids are excellent assistants in the flushing of pigments. Thus Prussian Blue (C.I. Pigment Blue 27) containing 70% of water is mixed with an equal weight of a mixture of dibutyl phthalate and castor oil. Then 2% (on the dry weight of the pigment) of 4-amino-1-methyl*cyclo*hexane is added and the whole mixed when in < 30 min. water begins to separate and the pigment is taken up by the carrier mixture. The addition of 4-amino-1-methyl*cyclo*hexane is repeated and the mixture thoroughly kneaded for 2 hr. until the bulk of the water has separated. The remaining water can easily be removed in vacuum at 40–60°c. The product is suitable for incorporation in inks and lacquers. C.O.C.

Fluorescent Dyed Resinous Pigments
Switzer Brothers *BP* 786,678

Modification of *BP* 733,856 (J.S.D.C., 71, 627 (1955)). Instead of dissolving or dispersing the dye in the aqueous solution of the alkyd resin, the resin may be first precipitated and the dye added afterwards. This yields excellent dyed resinous pigments. C.O.C.

Iridescent Flake for use in Plastics
Rainbo-Cel. *BP* 786,667

Incorporation into a plastic of flake including at least two metallic films produces an iridescent product which is as iridescent as the flake itself. The flake is made up of a plastic base one or both surfaces of which is coated with at least two metallic films separated by a layer of a transparent plastic. These coatings are arranged so that one surface of the flake is formed by a light transmissive layer overlying a light transmissive film or *vice versa*. C.O.C.

Improving the Dispersibility of Pigments
T. A. Te Grotenhuis and General Tire & Rubber Co. *USP* 2,751,369

The pigments are treated with a liquid organosilicon compound having directly attached to an Si atom at least

one water-hydrolysable group and at least one C atom, preferably removing non-silicon-containing hydrolysis products, e.g. HCl, formed by the reaction between the organosilicon compound and either adsorbed film of moisture or hydroxy or carboxylic acid groups on the surface of the pigment particles. C.O.C.

Bleed Resistance of Printing Ink Pigments (V this page)
Powdered Mica (C.I. Pigment White 20) and its Use in Paints (V this page)
Light Absorption of some Cyanine Dyes adsorbed on Regenerated Cellulose Film (VIII p. 207)
Dyeing Polymers of Acrylonitrile or Asymmetric Dicyanoethylene (VIII p. 208)
Basic Dyes for Dyeing Acrylic Fibres (VIII p. 209)
Magenta Colour Couplers (IX p. 211)
Fast Sulphur Black F (C.I.26990) as an Indicator for the Titration of Copper with Ethylenediaminetetraacetic Acid (XIV p. 217)
Complexometric Determination of Iron in the presence of Variamine Blue (C.I. Azoic Diazo Components 22, 35, and 47) Indicator (XIV p. 217)
Photometric Determination of Thallium with Rhodamine B (C.I. Basic Violet 10) (XIV p. 217)
Determination of Quercetin (C.I.75670) and Rutin (C.I.75730) (XIV p. 218)
Crystallisation of Organic Pigments (XIV p. 218)
Determination of the Specific Surface of Leafing Aluminium Flake Pigments (C.I. Pigment Metal 1) in Pastes (XIV p. 218)
Differentiation of Titanium Dioxides (XIV p. 218)

V—PAINTS; ENAMELS; INKS

Bleed Resistance of Printing Ink Pigments

T. E. Ludwig

Amer. Ink Maker, **35**, (5), 43–5 (1957): *Chem. Abs.*, **51**, 15966 (25 Oct. 1957)

Draw-downs, on bond paper, of dispersions of 51 organic pigments, were immersed in 16 test media. The results are given in tables. C.O.C.

Dyes for Ball Point Pen Inks

N. L. Anderson

Amer. Ink Maker, **35**, (2), 38–9, 63, 65 (1957): *Chem. Abs.*, **51**, 17195 (20 Nov. 1957)

Lists of suitable dyes are given. C.O.C.

Effect of the Anion on the Drying Properties of Oils catalysed with Cobalt Salts

A. Doadrio and R. Montequi

Grasas y Aceites (Seville, Spain), **8**, 76–7 (1957): *Chem. Abs.*, **51**, 15966 (25 Oct. 1957)

The catalytic effect of Co on drying of drying oils is decreased by increased complexing power of the anion, 1-nitroso-2-naphthol almost destroying the catalytic action. The effect of 1:10-phenanthroline is negligible. C.O.C.

Powdered Mica (C.I. Pigment White 20) and its Use in Paints

G. Genin

Peintures, Pigments, Vernis, **33**, 631–6 (1957)

Use of mica both as an inert extender and as a functional pigment in the formulation of various types of oil and aqueous latex paints is reviewed. Examples are given. C.O.C.

Coloured Emulsion Paints for Outside Use

A. D. Hibberd

Verfkroniek, **30**, 165–170 (1957): *Chem. Abs.*, **51**, 17193 (20 Nov. 1957)

Fading of pastel-coloured emulsion paints can be checked in two ways: (1) use of a chalk-resistant rutile TiO_2 as basic pigment at a reduced pigment volume concentration to reduce chalking to a minimum. Organic or inorganic pigments can be used, if they are fast to light and not subject to the so-called chemical fading. Such paints retain their colour for a long time, but when chalking becomes considerable the organic pigments fade. Retention of dirt is their main disadvantage. (2) Self-cleaning paints obtained by controlled chalking, the type of TiO_2 and the quantity must be chosen to suit the environment in which they are to be used. Organic pigments are unsuitable for colouring and the inorganic must be carefully chosen. Although paint with inorganic pigments cannot exactly match the colour of the original paint, yet when it chalks it does remain coloured, whereas a paint coloured with an organic pigment on chalking to the same degree turns white. C.O.C.

Behaviour of some White Emulsion-paint Systems during Natural Weathering

A. D. Hibberd

Verfkroniek, **30**, 155–164 (1957): *Chem. Abs.*, **51**, 17193 (20 Nov. 1957)

Paints based on poly(vinylalcohol) (I), alkyd (II), polystyrene (III), and styrene-butadiene (IV) emulsions and TiO_2:binder ratio 1:1 were tested on wood and concrete. On wood, American-type house paints gave most protection, followed closely by II and I, especially when put on top of a white lead primer. I had the best appearance. III and IV did not appear satisfactory for outdoor use. For vertical surfaces the self-cleaning properties of a I paint at pigment-volume concentration 22% and using a chalk-resistant TiO_2 pigment, is not good enough except in a very clean atmosphere. This can be controlled either by using a higher pigment/binder ratio, up to 29% pigment-volume concentration, a rutile pigment of slightly lower chalk-resistance, or by replacing part of the rutile by anatase. Rough-cast concrete retains more dirt than smooth concrete and for self-cleaning requires a paint chalking more freely than smooth surfaces do. ZnS is unsuitable as basic pigment for emulsion paints for outdoor use. C.O.C.

Mathematical Approach toward proper Pigment/Paint Ratios

J. J. Taylor

Paint Ind. Mag., **72** (7), 8, 13, 61 (1957)

Electrostatic Applications of Polychromatic Coatings

G. E. F. Brewer

Paint Varnish Production, **47**, (8), 44–5, 96 (1957): *Chem. Abs.*, **51**, 15146 (10 Oct. 1957)

The effects and control of frictional electrification are considered. Electrification can be controlled by use of properly formulated thinners, examples of which are given. When frictional electrification is minimum the metallic effects of polychromatic finishes are more uniform. No correlation between electrostatic effects of various solvents and coating compositions was found. C.O.C.

PATENTS

Ink for Ball Point Pens

J. S. Staedtler *BP* 786,777

The ink comprises a water-insoluble pigment, a water-soluble organic thickening agent, a water-soluble solvent and an electrolyte. The latter is capable of settling in the surface written on to produce a latent script image which after erasure of the writing can be rendered visible by chemical treatment. C.O.C.

Printing Inks for High Speed Printing

Sun Chemical Corpn. *USP* 2,750,296

Use as a vehicle of an oil-soluble resinous binder dissolved in mineral oil and mixed with a long chain aliphatic amine bentonite (Alk of 34 C) (product obtained by treating sodium bentonite with a suitable amine) yields an ink which has little or no flying tendency under high speed printing conditions. C.O.C.

Inks for Printing on or Dyeing Plasticised Polyvinyl Acetal Sheeting

DuP *BP* 787,161

A mixture of an oil-soluble dye, a polyvinyl acetal resin (e.g. poly(vinyl butyral)), a plasticiser and a volatile solvent, is used. Applied by photogravure (using a 50–250 screen size) a mottled print is obtained which on being kept at 60°C. for 3–5 days becomes transformed into a smoothly distributed tinting. C.O.C.

Wrinkle Varnishes or Paints

Council of Scientific and Industrial Research, India *USP* 2,749,247

Coatings having uneven wrinkled surfaces of regular pattern are obtained by use of medium or long oil length varnishes or paints, prepared from mixtures of oils and resin, the wrinkling oils used being either animal or vegetable oils which have conjugated double bond acids as components, e.g. kamala or tung oil. C.O.C.

Aqueous Polymer Dispersions as Base for Water Paints

Dow Chemical Co. *BP* 786,146

Aqueous interpolymer dispersions of exceptional stability against freezing or addition of inorganic salts are

obtained by heating a mixture of a non-ionisable vinyl aromatic compound, a water-soluble salt of a vinyl sulphonic acid, a polymerisation catalyst and at least enough water to dissolve the sulphonic acid. C.O.C.

Aqueous Paint Emulsions
Firma Paul Lechler *BP* 788,160

A bituminous binding agent is emulsified with an inorganic colloid, e.g. bentonite, in presence of 0·1–2·0% of a water-soluble siliconate. Presence of the siliconate greatly increases the resistance to water of coatings formed from the paint. C.O.C.

Dry Paint Mixture
N. G. Cadegans *USP* 2,749,249

Loose clay is baked for 45 min. at ≮ 500°F. and is then thoroughly washed and mixed with water until a liquid "batter" is formed. This batter is drained into a tank, stirred violently and after 1 min. the "cream" first formed is drained into another tank. In this tank the coarser material is allowed to settle out of the cream which is then removed to dehydrating pans. The water which separated from the cream during its stay in these tanks is drained off by means of spigots in the sides of the tanks. The dehydrated cream is then ground to form a dry paint mixture which only needs oil adding to form a paint. C.O.C.

Water Plastic Paint
A. G. Elliott *BP* 786,190

A washable water plastic paint consists of a mixture of 93% of carbonate of lime (C.I. Pigment White 18), 6·5% of animal glue and 0·5% of paraformaldehyde. C.O.C.

Fungicidal Paints
Ethyl Corpn. *BP* 786,792

2:4-Dichloro-6-(aryloxy-*s*-triazines, 2-chloro-4:6-(aryloxy)-*s*-triazines, 2:4-dichloro-6-(arylamino)-*s*-triazines and 2-chloro-4:6-(arylamino)-2-triazines are excellent fungicidal agents for use in paints, even 0·25% by wt. of the total paint formulation giving effective control over common paint mildewing organisms, e.g. *Aspergillus niger*, *A. oxyzae*, etc. C.O.C.

Flame-resistant Film-forming Composition
Celotex Corpn. *BP* 785,977

A paint for application to paper, boards, etc. consists of (*a*) powdered aminoaldehyde resin, oil seed meal or casein, (*b*) ammonium phosphate, (*c*) a film-forming water-insoluble amino-aldehyde resin soluble in an organic solvent in combination with an alkyd resin, (*d*) an organic solvent for (*c*) but not for (*a*) and (*b*), and (*e*) any desired pigment. C.O.C.

Durably Elastic Stoving Compositions
Chemische Werke Hüls *BP* 786,406

Durably elastic stoving coating compositions are obtained from unsaturated polyester resins, fillers, pigments, etc., by adding benzyl alcohol or one of its derivatives. C.O.C.

Monoazo Compounds as Absorbents for Ultraviolet Radiation (III p. 191)
Flushing Pigments or the Like (IV p. 202)
Iridescent Flake for Use in Plastics (IV p. 202)
Protective Films having a Bright Reflective Metallic Lustre (XIII p. 216)
Determination of the Specific Surface of Leafing Aluminium Flake Pigments (C.I. Pigment Metal 1) in Pastes (XIV p. 218)

VI—FIBRES; YARNS; FABRICS

Chemical Production of Cottonised Fibre in Pressure Boilers
K. Jach

Przemysł Włókienniczy, (3), (1956), *Biul. Inst. Przem. Wlok. Lykow.*, pp. 5–6: *Polish Tech. Abs.*, (25), 147 (1957)

In the chemical production of cottonised fibre from green-fibre flax tow in pressure boilers, the following conditions were maintained throughout: NaOH concn. 150 g. per kg. of raw material, liquor ratio 10:1, boiling time 2 hr. Optimum pressure for cottonisation of flax fibres was found to be 2–3 atm. Increased pressure does not justify any substantial reduction in NaOH concn. without harm to the process. On the contrary, increased NaOH concn. reduces the amount of impurities and enhances the divisibility of the fibre. Optimum amounts of NaOH vary in pressure cottonisation between 80 and 125 g. per kg. of raw material, depending on the kind of material as well as on the quality of the cottonised fibre. C.J.W.H.

Chemical Methods of Producing Cottonised Fibre in Pressure Vessels
K. Jach

Prace Inst. Przem. Wlok. Lykow, (2), (12), *Warszawa*, *WPLiS*, 4 (1956): *Polish Tech. Abs.*, (26), 139 (1957)

Tests for obtaining various sorts of cottonised fibre on a technical scale were made together with an investigation of the influence of pressure on the cottonisation process, and the influence of concentration of sodium hydroxide and of the amount of soap, zinc, and aluminium salts, sodium sulphide, etc. in the cottonisation bath. Good results were obtained with a pressure of 2–3 kg./cm.² (at a temp. of 133–143°c.). The optimum amount of hydroxide varies from 60 to 125 g. per kg. of raw material, depending on the kind of material and the desired degree of partition into the elementary parts. An addition of soap to the cottonising bath in amounts of 2–10 g. per kg. of raw material, as also of small amounts of zinc chloride or aluminium sulphate (about 1 g. per kg. of raw material) is advantageous. When cottonising green fibre, an addition of a certain amount of sodium sulphide is recommended. A method of bleaching cottonised fibre using sodium hypochlorite, on the technical scale, is worked out. C.J.W.H.

Chemical Methods of Obtaining Cottonised Fibre in Non-pressure Vessels
Z. Sluchocka

Prace Inst. Przem. Wlok. Lykow, (2), (12), *Warszawa*, *WPLiS*, 7 (1956); *Polish Tech. Abs.*, (26), 137 (1957)

An investigation on the influence of different chemical agents, and of physical and chemical parameters on the cottonisation process in non-pressure vessels of biological and green tow from fibre and oil flax. In particular, the effects of sodium hydroxide, sodium bisulphite, metallic ions, and surface-active compounds were examined. An addition of bisulphite and soaps is advantageous to the quality of cottonised fibre. In the case of cottonised green fibre, the optimum concentration amounts to 150–200 g. of NaOH per kg. of fibre, the optimum time of boiling being 90 min., 25–30 g. of $NaHSO_3$ and 1–3 g. of soaps. The optimum concentration for cottonisation of biological tow amounts to 150 g. of NaOH per kg. of fibre with an optimum time of boiling of 60 min. The amount of sodium hydroxide may be decreased by leaving the hot fibres in the settling tank after boiling. The optimum ripening time was found to be 4 hr. for cottonised fibre from biological fibre, and 8 hr. for cottonised fibre from green fibre. The best results were obtained from washing with hot water. C.J.W.H.

Problems of Research in the Chemistry of Jute Cellulose
W. G. Macmillan

Indian Textile J., **67**, 338–343 (March 1957)

Properties and Utilisation of Partly Acetylated Cotton
M. Zilahy and L. Oswald

Magyar Textiltechnika, (6), 204–207 (1956): *Hungarian Tech. Abs.*, **9**, (2), 57 (1957)

If the cotton is acetylated to a degree at which the amorphous parts are completely transformed into triacetate, the fibres become pliant and are left somewhat sticky by the washing process subsequent to acetylation. This effect increases the breaking strength. Elongation will be slightly less than with cotton yarn. C.J.W.H.

Chemical Modifications of Natural Fibres
E. M. Buras

Amer. Dyestuff Rep., **46**, 929–930 and 939–940 (2 Dec. 1957)

Chemical modification of wool and cotton of commercial interest are discussed. Cotton partially acetylated with acetic anhydride and, in some cases, perchloric acid has enhanced rot, heat, and acid resistance. Dyed with certain vat dyes, it is especially resistant to sunlight. Cotton which has been virtually completely acetylated with acetic anhydride has better tear and abrasion resistance than synthetic-solvent-spun cellulose triacetate fibres.

Wool acetylated with acetic anhydride has a lower dye affinity and an increased mildew resistance compared with untreated wool, but the esterification is difficult to control. Cotton can be esterified with methanesulphonyl chloride; if this is followed by substitution with bromine or iodine, the fibre produced is flame-resistant. Cotton cyanoethylated with acrylonitrile has modified dyeing properties. Acrylonitrile can also be polymerised within the fibre. Both processes improve the heat, rot, acid and weather resistance of the fibre. The treatment of cotton with chloroacetic acid, aminoethylsulphuric acid, formaldehyde, and phosphoric acid is also mentioned. Sulphamic acid, chlorine, and reducing agents followed by alkyl dihalides are used to modify wool. P.T.S.

Phase Transition Study on the Mercerisation of Cellulose
Y. Tsuda

Bull. Chem. Soc. Japan, **30**, 589–593 (Sept. 1957)

Measurements were made of the transition from cellulose I to cellulose II for cotton linters pulp and sulphate and sulphite wood pulps, when treated with NaOH soln. of 8–20% concn. at 20° and 45°c. X-Ray diffraction curves of the treated pulps were measured, and the degree of transition obtained from the intensity ratio $I(10\bar{1})/I(002)$, which was compared with the same ratio for known mixtures of celluloses I and II from the three pulps. The two wood pulps show identical behaviour, and the cotton pulp is more resistant to alkali. In all cases increasing temp. decreases the efficiency of mercerisation. Comparison with lateral-order distribution measurements (Y. Tsuda and S. Mukoyama, *ibid.*, **30**, 271 (1957)), show that this changes simultaneously with phase transition and does not precede it. A.J.

Structure of Viscose Rayon—I and II
E. Turska, B. Antczak, J. Cypryk, T. Skwarski, and M. Kauczynska-Wolfram

Zesz. Nauk. Politech. Lódz., No. 14 (*Włókiennistwo* 3), 3–32 and 33–47 (1957)

I—The following methods were used in the investigation of the structure of viscose rayon—(1) Sorption of iodine for the determination of crystallinity. (2) Determination of the anisotropy of swelling and refraction for the measurement of the orientation. (3) Staining with Victoria Blue and Chrysophenine G for the measurement of the thickness of the skin. Steamed and unsteamed yarns were used for the work. It was found that steaming increases the crystallinity but the ability to crystallise varies greatly and depends upon the finishing processes in general and drying in particular. Viscose dried in bulk shows irregular and decreased sorption of iodine. Crystallinity does not depend upon orientation. During spinning the crystalline regions are oriented more easily than amorphous regions. The longitudinal swelling is directly proportional to the moisture content in the yarn up to 30–40%. There is no change in the dimensions above this value. The cross-sectional swelling does not depend upon the moisture content of the yarn. A high anisotropy of swelling is due to a high degree of orientation. The thickness of the skin depends upon the time the yarn takes to pass through the coagulating bath in spinning and is directly proportional to it. It decreases the anisotropy of swelling, which is the measurement of the amorphous and crystalline regions, and depends upon the size of the amorphous regions. The increase in crystallinity decreases the wet stretch and the difference between the wet and dry stretch.

II—Measurement of the absorption of iodine by continuous-filament viscose rayon indicates clearly that the orientation of the yarn does not increase or promote its crystallinity. The refractive index of the continuous-filament yarn is directly proportional to the stretch, and is slightly increased by desulphurisation. The longitudinal swelling is also directly proportional to the water content in the yarn up to 25%. The cross-sectional swelling is not restricted by the water content. The thickness of the skin is directly proportional to the time of coagulation. T.Z.W.

Shape of Cross-sections of Viscose Rayon Fibre
S. Wydrzycki and Z. Cichowski

Przemysl Chemiczny, (8), 456–462 (1956): *Polish Tech. Abs.*, (25), 149 (1957)

Thermodynamic Properties of Secondary Cellulose Acetate–Solvent Systems
R. Jeffries

Trans. Faraday Soc., **53**, 1592–1600 (Dec. 1957)

Values of the free energy, heat, and entropy of dilution in phenol–cellulose acetate and acetone–cellulose acetate systems are calculated from vapour pressure and osmotic pressure data. Thermodynamic properties are qualitatively similar to those of other polar polymer–solvent systems. W.R.M.

Tendencies in Present-day Wool Research
H. Zahn

Textil-Rund., **12**, 611–622 (Nov. 1957)

Reviewed under the headings morphology, molecular form, supercontraction, chemical constitution, mol. wt., amino acids, dyeing theory, chemical modification, chemical testing, and degradation. S.R.C.

New Method of Examining Fibre Cross-sections by Electron Microscopy—Application to the Structure of Wool
P. Kassenbeck and M. Leveau

Bull. Inst. Text. France, (67), 7–18 (May 1957)

The fibre is embedded in polymethyl methacrylate, and sections are cut and polished with increasingly fine grades of emery. The section is then mounted in the centre of one of a pair of copper electrodes, and subjected to ionic bombardment for 5 min. by passing an alternating voltage of 3–4 kv. at a pressure of 5–7 cm. of mercury. An imprint of the surface is then taken in polystyrene. A carbon replica of the imprint is made, and the supporting resin dissolved. Examination of cross-sections of merino wool fibres by this method shows the marked morphological differences between ortho- and para-cortex. Pretreatment of the fibre with bromine water causes preferential swelling of the paracortex, which then possesses a submicroscopic appearance very similar to that of the orthocortex. It is suggested that at some stage in the biosynthesis of the fibre, swelling of the orthocortex alone occurs, possibly owing to osmotic effects linked with its comparatively late keratinisation. J.C.F.

Felting Properties of Wool and Animal Hairs
M. Leveau

Bull. Inst. Text. France, (67), 19–36 (May 1957)

After discussing the nature of felting and the morphology of animal fibres, the author reviews theoretical aspects of felting under the following headings—(*a*) influence of surface properties, (*b*) influence of the cortex—swelling and elastic properties, (*c*) influence of cortical asymmetry and crimp—spontaneous felting. J.C.F.

Polyamide Fibres—6,6-Nylon and 6-Perlon
P.-A. Koch

Textil-Rund., **12**, 685–700 (Dec. 1957): *Z. ges. Textilind.*, **59**, 777–786 (5 Oct. 1957)

Commercial names, history, manufacture of polymer, spinning, chemical constitution, properties, availability, and fields of application are tabulated. 229 references. S.R.C.

Polymerisation of ε-Caprolactam in Presence of Sodium and Carbon Dioxide in Solution and in Substance in Presence of Mixtures of Basic Activators
S. Chrzczonowicz

Zesz. Nauk. Politech. Lodz., No. 15 (*Chemia* 5), 65–92 (1957)

20 g. of ε-caprolactam and 120 g. of xylene were heated in N_2 until 20 g. of the solvent distilled over. 0·12 mol. of Na per mol. of ε-caprolactam was added. When the interaction of Na and the ε-caprolactam finished, CO_2 was passed at the rate of 40 ml./min., and the polymerisation was carried out at 142°c. and finished after 120 min., giving a product of D.P.200 in about 50% yield.

For polymerisation in substance 100 g. of ε-caprolactam was heated in N_2 to 250°c., 0·004–0·008 mole of Na per mole of ε-caprolactam pasted with xylene was added, and the mixture was heated gently to the boil simultaneously passing in CO_2 at the rate of 10 ml./min. After 20–30 min. thickening of the reaction mixture and a rise in temp. were observed. The polymerisation started at 264°c. and finished at 290°c. Similar work was done using as activators mixtures of NaOH and CaO and of NaOH and ZnO.

There are six different reactions which can take place simultaneously during the polymerisation. The factor

deciding the yield of the polymerisation in the solvent is the initial concentration of $-\overline{N\cdot[CH_2]_5\cdot CO}$ ions. The polymerisation reaction depends upon the concn. of OH^- ions, which must not exceed a maximum, because then hydrolysis of the amide would take place, which would stop the reaction or result in the formation of low-D.P. products. The most active catalyst for the polymerisation of the caprolactam in substance is a mixture of Na and CO_2 in xylene, because of its fine dispersion and the temp. of its addition (250°c.), which probably causes the evaporation of the H_2O formed. The more active influence of NaOH in the absence of dehydrating agents is also similarly explained. T.Z.W.

Fractionation of Ethylene Glycol Terephthalate
E. Turska and T. Skwarski
Zesz. Nauk. Politech. Lodz., No. 15 (*Chemia* 5), 21–28 (1957)

10 g. of the polymer prepared by the condensation of dimethyl terephthalate with ethylene glycol in the presence of Sb and Pb oxides as catalyst was purified by extraction with C_2H_5OH and $CHCl_3$ and dissolved in a 50 : 50 mixture of phenol and chloroform at 80°c. to form a 1% soln. *n*-Heptane was then added at 50°c. until turbidity occurred. After 6–10 hr. the liquid separated into two layers containing the polymers of lower and higher mol. wt. respectively. After the separation of the layers the polymer was precipitated from each soln. by the addition of C_2H_5OH, filtered, washed, and dried. The two fractions so obtained were treated in turn in the manner described above. In such a way 15 fractions were prepared. This method of fractionation gives reproducible results, is simple, and is relatively short. T.Z.W.

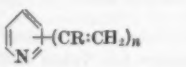
PATENTS

Spinning Variegated Filament Yarns
Rhodiatoce *BP* 784,839

A process for obtaining variegated filament yarns consists in feeding to a single spinneret two or more spinning solutions containing differently coloured pigments or dye intermediates at a low velocity to prevent intimate mixture of the spinning dopes. W.G.C.

Cellulose Acetate containing Vinylpyridines as Gas Fume Fading Inhibitors
Phillips Petroleum Co. *BP* 785,497

Fibres or films formed from cellulose acetate to which a compound of formula—



(R = H or CH_3; n = 1 or 2) or a polymer thereof, e.g. poly(2-methyl-5-vinylpyridine), yield dyeings which are faster to gas fume fading than are obtained on those formed from cellulose acetate in absence of such a compound. C.O.C.

Fibres from Cellulose Thiourethane-Acrylic Acid Derivatives
American Viscose Corpn. *USP* 2,748,010

Fibres formed from the products obtained by extrusion of an ether obtained by treating a cellulose thiourethane with an acrylic acid derivative have excellent affinity for both acid and disperse dyes. C.O.C.

Acetylation of Cotton with Acetic Anhydride Vapour (X p. 211)
Treatment of Silk Fibres with Diazomethane. I— Synthesis and Selection of the Solvent for Diazomethane (X p. 212)
Reducing the Water-imbibition of Regenerated Cellulose (X p. 212)
Effect of γ-Radiation on Cellulose (XI p. 214)
Rapid Method of Fractionation of Viscose Rayon and Cellulose of Low Degree of Polymerisation (XI p. 214)
Structure of Cellulose Triacetate (XI p. 214)
Optical Rotation and Infrared Spectra of some Polypeptide and Protein Films (XII p. 215)
Effect of Hydrogen Chloride on the Infrared Spectrum of Nylon (XIII p. 216)
Rendering Thermoplastic Materials Faster to Light (XIII p. 216)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Practical Aspects of Neutral Grease-wool Scouring
E. J. McNamara
Amer. Dyestuff Rep., **46**, 731–736 (7 Oct. 1957)

Historical review of scouring with synthetic detergents, and its advantages over soap and soda scouring. Anionic detergents have no great advantage over soap and soda; non-ionic detergents, usually of the alkylphenol–ethylene oxide type, are absorbed less by wool, and at pH 7 damage to wool is reduced. The counterflow of scouring liquor against the movement of the wool in the scouring train gives the best-quality wool and the easiest control. Wool grease from neutral scouring is darker, but the refining difficulties are being overcome. P.T.S.

Cleaning of Synthetic Fur-pile Fabrics
D. S. Lyle
Amer. Dyestuff Rep., **46**, P 699–P 705 (23 Sept. 1957)

Difficulties arise when synthetic fur-pile fabrics are dry-cleaned because the pile tends to bunch together ("tuft") or to be flattened. Investigations showed that dry-cleaning is feasible if the washer is not overloaded, otherwise the fabric may crease. Below 140°F. tumble-drying does not have adverse effects; after drying, a cold tumbler may improve the appearance of the cloth. Tests also showed that there was no connection between small amounts of water dissolved in the dry-cleaning solvent and the degree of tufting. The degree of tufting is proportional to the time of the dry-cleaning cycle. Further trouble arose when the dry-cleaning of imitation mink was attempted, and the stripes were found not to be fast to some dry-cleaning solvents. P.T.S.

Colour Fastness to Washing— Household Detergents
D. Cooper
Canadian Textile J., **74**, 58–59 (12 July 1957)

The effect of 14 household detergents, comprising built synthetic detergents, neutral synthetic detergents, and built soaps, was compared with that of soap in fastness-to-washing tests on 14 fabrics, by treatment in 0·5% soln. at 130°F., followed by rinsing. No noticeable difference was observed in change of colour, but some household detergents caused more staining, particularly on nylon. W.K.R.

Milling of Beaten and Woven Felts
H. Piaskowska
Prace Inst. Wlokien, (23), *Warszawa*, *WPLiS*, 20 (1956): *Polish Tech. Abs.*, (26), 147 (1957)

A number of tests of acid and alkaline milling enabled optimum parameters of the process to be determined. For the production of beaten felts of a high specific weight in an acid medium, the concentration of the sulphuric acid solution in the padding machine should be 2–2·8° Bé., the optimum values of the other parameters being— temp. of soln. 50–55°c.; rate at which the felt travels through the soln. 15–20 metres/min.; consumption of the solution in relation to the dry intermediate product 160–200%. In order to obtain woven felts weighing 300–1500 g./sq.m., optimum concentration of the solution should be 2+0·5°Bé. at a pH of 0·5–1·0; temp. of the solution 55°c.; consumption of the milling solution 100% in relation to the dry fabric. As regards an alkaline medium for beaten felts, the concentration of the solution in the padding machine should be 15+2 g. of 60% potassium or sodium soap and 3 g. of soda per litre at pH 9–10. The other optimum parameters are— temp. of the milling solution 50°c.; rate at which the felt is passed through the solution 15–20 metres/min.; consumption of the solution in relation to the dry intermediate product 160–200%. For white woven felts weighing 300–1500 g./sq.m., the composition of the solution should be 10–15 g. of 60% potassium or sodium soap and 3 g. of soda per litre at pH 9–10. The remaining optimum parameters are— temp. of the milling solution 50°c.; consumption of the solution in relation to the dry fabric 100%. C.J.W.H.

Carbonising Wool Stock— Improved Sulphuric Acid Method
Commonwealth Scientific and Industrial Research Organisation (Australia) Wool Science and Technology Report No. 1:
Canadian Textile J., **74**, 51–54 (1 Nov. 1957)

Recent work carried out by the Australian C.S.I.R. has shown that the addition of small quantities of surface-active agents to the sulphuric acid bath minimises loss in

fibre strength and improves the yield and the quality of the carbonised wool. A non-ionic agent used at the rate of ½ lb. per 100 gall. sulphuric acid, with a feed of ¼–½ lb. per 100 lb. wool treated was found to be very effective. Scouring of the wool before carbonising is advantageous. W.K.R.

Discoloration of Orlon Sweaters in Dry Cleaning
C. H. Bayley and A. S. Tweedie
Canadian Textile J., **74**, 64 (20 Sept. 1957)

Certain types of discoloration observed on dry cleaning Orlon garments were attributed to staining by dyes. It was found that certain basic and disperse dyes, used for dyeing Orlon, were soluble to an appreciable extent in the mixture of solvent, detergent, and water used in dry cleaning by the "charged-system" method. Dyes so dissolved caused appreciable staining of Orlon, which was not removed by rinsing in clean solvent. W.K.R.

Solvay Activated Hydrogen Peroxide Bleaching Process
W. R. Steele and S. M. Rogers
Amer. Dyestuff Rep., **46**, P 965–P 967 (16 Dec. 1957)

The sodium chlorite and chlorine dioxide bleaching processes need costly machinery and give rise to objectionable gases. The equipment for chlorine dioxide bleaching must be corrosion-resistant. Hydrogen peroxide has to be mixed with sodium silicate to control the release of oxygen during bleaching, and with caustic soda so that silica complexes shall not be precipitated on the fibres. In the Solvay process the cloth is saturated with sodium hypochlorite solution (1 g./litre, prepared by chlorinating caustic soda) for 1 min. It is then squeezed to approx. 100% wet-out, allowed to stand for 10–20 min., and, without washing, treated with hydrogen peroxide solution. The consumption of peroxide is greatly reduced in this process, and the water used to wash the cloth after bleaching need not be specially filtered or softened. Whiteness, whiteness retention, and absorbency are increased, fluidity and ash are decreased. The reaction involved is—

$$NaClO + H_2O_2 \rightarrow NaCl + H_2O + 2O$$

P.T.S.

PATENT

Bleaching of Polyacrylonitrile Fibres
Eastman Kodak Co. *USP* 2,751,277

Polyacrylonitrile fibres are readily bleached by 1–10% organic or inorganic acids at 20–100°c., the time needed being 1–3 hr. Oxalic is the preferred acid. C.O.C.

New Aspects of the Pad–Roll System (I p. 187)

VIII— DYEING

Photochemical Stability of Dyes in the Solid State
G. S. Egerton and A. G. Roach
Nature, **180**, 1349–1350 (14 Dec. 1957)

Polymer films were dyed with aminoanthraquinones, and films of the compounds on quartz obtained by vacuum deposition. Samples were sealed in quartz cells, through which dry oxygen or nitrogen was passed during exposure to radiation from a mercury-vapour lamp and while absorption measurements were made. The compounds were much more stable to the action of near ultraviolet radiation and visible light when present as films on quartz than as a dyeing on a polymer film. The effect of the presence or absence of oxygen also differs considerably between the solid state and dispersion in a polymer film. The photochemical stability is presumably dependent on the mode of attachment of the dye to itself or to polymer. It is suggested that intermolecular complexes are formed in the solid state and contribute to stability. W.R.M.

Factors Influencing Levelness in Dyeing
I. Selló and A. Sárdi
Magyar Textiltechnika, (2), 73–76 (1956): *Hungarian Tech. Abs.*, **9**, (1), 20 (1957)

The purpose of the investigations was to examine the rôles of dye uptake from a partly exhausted dyebath and of dye migration on attaining levelness in dyeing. The experiments proved that the subsequent levelling of an unlevel dyeing results chiefly from subsequent uptake of dye from the dyebath, and arises only to a smaller extent from migration of the dye. Lengthy periods of dyeing and of migration increase levelness because of migration, while increase of the dyestuff concentration promotes the subsequent dyestuff uptake. The investigations were also carried out in the presence of an anionic and a non-ionic levelling agent, the former being a salt-free fatty alcohol sulphate, and the latter Peral O. Under the experimental conditions employed the retarding effect of these anionic and non-ionic agents promotes level dyeing. C.J.W.H.

Effect of Fixing Agents on the Fading of Dyed Regenerated Cellulose
Y. Ishii
Sen-i-Gakkaishi, **13**, 110–115 (1957): *Chem. Abs.*, **51**, 15116 (10 Oct. 1957)

Regenerated cellulose film dyed with Chrysamine G (C.I. Direct Yellow 1), Direct Brown M (C.I. Direct Brown 2), Oxamine Brown G (C.I. Direct Brown 17), Japanol Copper Blue 2B (C.I. Direct Blue 151), Benzo Cuprol Blue FBL (C.I. Direct Blue 158) and Japanol Brilliant Blue RWL (C.I. Direct Blue 22) and then treated with dicyandiamide-HCHO resin, Sapamine KW or a cation surface activator had λ_{max} of the absorption spectra shifted towards shorter wavelengths and the dyed films faded rapidly. Adding $CuSO_4$ to the fixing bath minimised such fading although it did not affect the deformation of the spectra. Films dyed with Cu blue dyes showed a new weak absorption on the red side of λ_{max}, which, however, was extinguished by the fixing agents or by exposure to ultraviolet radiation (which apparently split the H bonds between the cellulose chain and dyes and deposited the dyes on the films). C.O.C.

Light Absorption of some Cyanine Dyes adsorbed on Regenerated Cellulose Film
G. L. Szepesy
Acta Univ. Szegediensis, Acta Phys. et Chem. [N.S.], **2**, 140–8 (1956): *Chem. Abs.*, **51**, 15272 (25 Oct. 1957)

The dyes used were: 5-[2-(3-ethyl-2-benzoxazolinylidene)ethylidine]-3-methyl-rhodamine (I), 3-methyl-5-[2-(3-ethyl-2-benzoxalinylidene)ethylidene]rhodamine, 3-methyl-5-[2-(3-ethyl-2-benzoxazolinylidene)ethylidene] rhodamine (II), 1:1′-ethyl-β-naphthoxazolocarbocyanine iodide (III), 1:2-diethylbenzoxacarbocyanine iodide (IV), 4-[3-ethyl-2-benzothiazolinylidene)ethylidene]-3-methyl-1-phenyl-5-pyrazolone (V) and 3-methyl-5-[2-(3-ethyl-2-benzothiazolinylidene)ethylidene]rhodamine (VI). The absorption spectra of their alcoholic solutions and those of their dyeings on regenerated cellulose strips showed that the absorption bonds in the adsorbed dyes had shifted to longer wavelengths than those of the dyes in solution. The order of the shift was VI > I = III > II > IV > V. Similar shifts in crystals and in conc. soln. have in the past been ascribed to polymerisation. The flat dye molecules are presumed to have edge-on orientation in the adsorbed layer. C.O.C.

Effect of Dyeing Conditions on the Quality of Wool Fibre
K. Janiszewski
Przemysl Włókienniczy, (6), 280–285 (1956): *Polish Tech. Abs.*, (27), 141 (1957)

The author discusses the effect of various methods of dyeing on the quality of wool fibre, analysing in detail the effect of varying pH in particular dyebaths. The wool substance is seriously affected when the solution contains a considerable quantity of electrolytes. The loss in breaking strength is least at pH 3·5, viz. below the isoelectric point for wool at pH 4·9, which is in agreement with the literature. Actual practice has shown that it is not necessary to adhere rigidly to the optimum pH. When Neopalatin dyes are used, the pH range may, without fear of injuring the fibre, be set at 2–7 for various methods of dyeing. In the case of metal-complex dyes, wool may be dyed in media ranging between strongly acid and neutral. C.J.W.H.

Dyeing of Wool, Hair, and Polyamide Fibres with Metal-complex Dyes
E. Schönpflug
Amer. Dyestuff Rep., **46**, 851–858 (18 Nov. 1957)

Translation of paper in *Textil-Praxis*, **12**, 70–79 (Jan. 1957)— see J.S.D.C., **73**, 183 (April 1957).

Diffusion of Acid Dyes in a Polyamide Fibre

T. Shimizu and U. Miyaoka

J. Soc. Textile Cellulose Ind. Japan, **13**, 553–559 (Aug. 1957)

The diffusion coefficients of the purified dye acids of three acid dyes (C.I. Acid Reds 88, 13, and 27) in Amilan were determined by the two methods, viz. use of Hill's equation and microscopic measurement of the distance of dye penetration, and the limits of application of these methods are discussed. The diffusion coefficients of these dyes in the unstretched fibre are all about ten times as large as those in the stretched fibre, and it appears that differences in the fine structure of the fibre greatly affect the diffusion coefficient. With increasing sulphonation, the diffusion coefficient of an acid dye in Amilan decreases, while the activation energy of diffusion increases. The authors have derived a simple equation relating the time of half-dyeing for Amilan in terms of the diffusion coefficient D (in sq.μ/min.) and the fibre denier d—

$$D = \frac{d}{0{\cdot}511t_{\frac{1}{2}}}$$

C.J.W.H.

Interfacial Film Phenomena in the Dyeing of Cellulose Acetate

J. H. Skinkle and E. C. Sherburne

Amer. Dyestuff Rep., **46**, 749–760 (21 Oct. 1957)

When a dispersion of 1-ethylamino-4-anilinoanthraquinone in water is shaken with amyl acetate, the amount of dye lost by the aqueous phase is not equal to that gained by the amyl acetate— there is an unexpectedly high concentration of dye at the interface. A similar phenomenon is known to occur when cellulose acetate is dyed with disperse dyes— the concentration of dye is higher at the cellulose acetate–water interface than elsewhere. The effect can be studied by calculating the amount of dye at the interface after different times from the exhaustion of the dyebath and the amount of dye on the fibres after rinsing in ice-cold water. The amount of dye at the interface rises to a maximum and then falls off. At about the time when the dye concentration at the interface is a maximum the dye uptake by the fibre also appears to have reached a maximum, but this turns out to be a false maximum, since dye uptake proceeds a short time later by, it is suggested, a different mechanism. Up to the apparent maximum dye uptake, dye molecules may be hydrogen-bonded to acetyl groups. Afterwards unacetylated hydroxyl groups may form hydrogen bonds with dye molecules. This suggestion is supported by a calculation of the relative volumes of the acetylated and unacetylated parts of the fibre which is in line with previous estimates. Experiments showed that concentrated interfacial dye films are not formed in the dyeing of wool or viscose rayon. P.T.S.

Dyeing of Hydrophobic Fibres. I— Effect of Acids and Swelling Agents on the Dyeing of Orlon 42 with an Anionic Azo Dye

J. H. Skinkle and A. A. Denio

Amer. Dyestuff Rep., **46**, P 706–P 708 (23 Sept. 1957)

Orlon 42 is a polyacrylonitrile fibre copolymerised with a small amount of basic monomer, probably vinylpyridine. Its rate of dyeing can be increased by using low pH, high temperatures or swelling agents. The same dyebath exhaustion is obtained using 5% formic acid (pH 3) or dilute HCl at pH 3. Formic acid and acetic acid adjusted by dilution to pH 3·45 cause equal exhaustion. Equimolar formic acid buffered to the pH of acetic acid with sodium formate causes a greater dyebath exhaustion, and thus formate ions or un-ionised formic acid appear to swell Orlon. For dyeing blends with cellulose fibres the use of formic acid at pH 3 would reduce damage. Ammonium thiocyanate assists dyeing by reducing the negative zeta potential of the fibre and by causing some swelling. Formaldehyde with hydrochloric acid decreases dyebath exhaustion; added hydroxylamine hydrochloride has no significant effect. Emulsified dimethylaniline can cause an increase or a decrease in dyebath exhaustion depending on its concentration. The effect is recorded with urea. Acetamide causes an increase in dyebath exhaustion. P.T.S.

Use of Colouring Ingredients in Fatty Food Products. Their Physiology, Chemistry, and Stability

J. J. Geminder and E. E. MacDonongh

J. Amer. Oil Chem. Soc., **34**, 314–318 (1957): *Chem. Abs.*, **51**, 12369 (25 Aug. 1957)

The colour stability of crystalline ethylbixin (I); I in cottonseed oil; I with added vitamin A (II) in cottonseed oil; II with β-carotene (III) in cottonseed oil; I, III, I + III, FD&C Yellow 3 (C.I. Food Yellow 10) and FD&C Yellow 4 (C.I. Food Yellow 11) in margarine was studied over several months' storage. In some cases effect of presence of Cu and sunlight was also studied. I and III to which II may be added were quite stable in margarine. In frying fats and popcorn oils only C.I. Food Yellow 10 and 11 are completely stable. C.O.C.

PATENTS

Pigment Padding of Vat Dyes on Cellulose Textiles

ICI *BP* 787,343

Carrying out reduction in presence of anthraquinone-2-sulphonic acid speeds up reduction, effects economy in a reducing agent, and gives better colour value. C.O.C.

Level Dyeings by the Pad-Steam Process

Kalle & Co. *BP* 788,369

Addition of water-soluble alkali metal salts of starch glycollic acid ether to the dispersion of vat dye used much reduces the tendency of the dye to migrate during drying and so results in more level dyeing. The addition also imparts stability to the dispersion of dye against settling out on standing. C.O.C.

Dyeing with Sulphur Dyes

CFM *BP* 787,878

The material is impregnated in absence of Na_2S, a reducing agent or caustic alkali, with a water-soluble reaction product of a sulphur dye with sulphurous acid, and is then heated to fix the dye. Thus cotton cloth is impregnated with an aqueous solution of the product obtained by treating C.I. 53721 with sodium sulphite, squeezed and then steamed for 5 min. at 110–115°C. It is then rinsed with water, treated with permethylated polyethylene imine for 3 min., rinsed and dried. This yields an intense claret of good fastness properties. C.O.C.

Colouring Acetate Fibres

T. E. Marchington & Co. *BP* 787,393

Good colorations are speedily obtained on ordinary cellulose acetate fibres and on cellulose triacetate fibres, by impregnating with dye liquor, drying and then treating with dry heat for 30–15 sec. at 170–210°C. Thus plain-weave acetate rayon cloth is impregnated with Serisol Brilliant Blue BG 300% (C.I. Disperse Blue 3) (30 g.), 5% aq. gum tragacanth (90 g.), and water (800 c.c.), dried, heated for 22 sec. at 185°C., soaped, rinsed in cold water, and dried to yield an excellent blue dyeing. C.O.C.

Dyeing Polyacrylonitrile Fibres

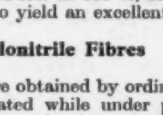
DuP *USP* 2,750,250

Level dyeings are obtained by ordinary processes if the fibres are first heated while under pressure or tension. Thus thoroughly scoured polyacrylonitrile taffeta is tenter dried at 260°F. and then passed under tension over six heating-setting cylinders at 380°F. at a speed which gives a total contact time of 10 sec. On dyeing at 205°F. in an open beck with Celanthrene Pure Blue BR8 400 (C.I. Disperse Blue 1), a level dyeing is obtained free from streakiness whereas cloth not so treated is dyed very unevenly with much streakiness and weft bars. C.O.C.

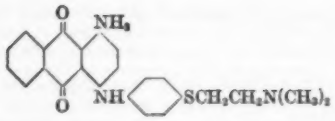
Dyeing Polymers of Acrylonitrile or Asymmetric Dicyanoethylene

FBy *BP* 788,708

Violet to greenish-blue dyeings on polymers based on acrylonitrile or *asymm.* dicyanoethylene are produced in boiling dyebaths (liq. ratio 40 : 1) containing an anthraquinone dye (1% on wt. of material), 30% acetic acid (3%), and Na acetate (1·5%). Alternatively, dyeing may be carried on at temperatures above 100°C. in closed vessels. The dyes used are obtained by condensing, e.g. halogenoanthraquinones, which may be further substituted, with amines of formula —



(R^1 and R^2 = H or Alk, and together with the N atom may form a ring; Z = aliphatic chain which may contain hetero-atoms such as O, S, NR or SO_2; Y = one or more subst. such as Hal, OH, OAlk, NH_2), e.g. the blue dye—

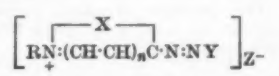


15 other examples are given. The dyeings obtained have good wet and light fastness. E.T.

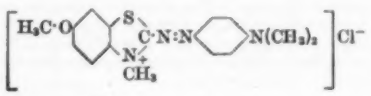
Basic Dyes for Dyeing Acrylic Fibres

BASF *BP* 787,891

Very fast brilliant dyeings are obtained by use of basic dyes of formula —



(R = Alk, aralkyl, Ar or *cyclo*alkyl; n = 0 or 1; X = divalent atom or group to complete a 5- or 6-membered ring; Y = radical of an aromatic amine or enamine capable of being azo-coupled; Z = anion). Thus polyacrylonitrile fibre is dyed a very level, pure blue with the dye



from an acetic acid bath. C.O.C.

Synthetic Resinous Binders for Pigment Padding and Printing Compositions

Rohm & Haas *BP* 786,805

Use of an aqueous dispersion containing (1) a low mol. wt. formaldehyde condensate of urea, a triazine or a biguanide, and (2) a water-insoluble linear polymer of monoethylenically unsaturated molecules comprising 0·5–7·5% of a monomer containing at least one COOX group (X = H, NH_4 or alkali metal) in pigment printing pastes, yields dyeings and prints fast to washing and dry-cleaning. Thus Monastral Fast Blue BFP (C.I. Pigment Blue 15), dimethylol-*NN'*-ethyleneurea, pyridine hydrochlorate and water-soluble hydroxyethyl cellulose are made into a paste with an aqueous emulsion of a copolymer of *n*-butylacrylate and methacrylic acid. This paste is padded into cotton cloth, dried and baked at 300°F. for 10 min. This gives dyeings of good fastness to rubbing, washing, and "cyclic ageing", i.e. exposed in a Fade-Ometer and then given a washing test. C.O.C.

Staining Wood to resemble Walnut

S. Cohen and P. Maurice *BP* 788,863

Tchitola wood (*pterygopodium oxyphyllum*) is made to resemble walnut by staining it with an aqueous solution of an iron salt. C.O.C.

New Aspects of the Pad–Roll System (I p. 187)

Application of Fluid Beds to Textile Processing (I p. 188)

Dyeing and Printing Cellulose Acetate, Nylon, Polyester Fibres or Films, and Cyanoethylated Cellulose (III p. 190)

Inks for Printing on or Dyeing Plasticised Polyvinyl Acetal Sheeting (V p. 203)

Colour Fastness to Washing— Household Detergents (VII p. 206)

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Pigmented Prints, Impregnations and Coatings on Fibrous Materials (IX p. 210)

Microdesorption Method for Determining the Adsorption Equilibrium and Heat of Dyeing (XIV p. 219)

IX— PRINTING

NN-Dehydroanthraquinoneazine in Printing on Cotton Fabrics

I. Jakobson and W. Józefowicz

Przemysł Włókienniczy, (1), 23–28 (1956): *Polish Tech. Abs.*, (25), 137 (1957)

The use of helianthrene (indanthrone C.I. Vat Blue 4) for printing on cotton fabrics has thus far presented a number of difficult problems as regards fixation of the dye on the fibres, brightness of colour, and proper levelling. The most suitable composition of the printing paste, and conditions for printing with paste containing the dye, have been determ ed. The printing paste was prepared without preliminary reduction. The optimum amount of the reducing agent (Rongalite) was set at 20 g./kg. calculated as solid product. Since soda lye contained in the printing paste was found to have a favourable effect, the amount of the lye was set at 250–320 g./kg. NaOH 50° Bé., as in the case of printing on cotton fabrics. In order to stabilise the process, the printing paste should contain 4–5 g./kg. Nitrol S against 100–150 g. of dye (20% paste) in 1 kg. of the paste. In view of the considerable content of soda lye, yellow dextrin should be used as a thickening agent. C.J.W.H.

Felt Printing

K. Muszkat

Przemysł Włókienniczy, (1), (1956), *Biul. Labor. Kolorystyczn.*, pp. 1–2: *Polish Tech. Abs.*, (25), 139 (1957)

Successful attempts to print felt products (slippers, scarves) made of coloured rag tearings have been made. Prior to printing, the products were stripped by means of hydrosulphite with addition of a stabilising agent in an acid medium. Stencil and screen methods were used in the printing tests. The gum used as thickening agent in the printing paste was obtained by dextrinating wheat flour. Printing pastes containing acid dyes were acidified with acetic acid; in the case of direct dyes the printing paste contained borax and sodium chlorate. It was established that screen printing on felt is more suitable for mass production than the stencil method, which requires more paste and more labour. The paste on the printed felt was dried and steamed for 1·5–2 hr. at an excess pressure of < 0·3 atm., and under continuous steam flow. After steaming, the felt was rinsed in water, dried, and pressed. C.J.W.H.

Nature of Photographic Sensitivity

J. W. Mitchell

J. Phot. Sci., 5, 49–70 (1957): *Chem. Abs.*, 51, 14453 (10 Oct. 1957)

In Ag halides adsorption of a light quantum forms a photoelectron and a positive hole, which must be prevented from recombining if a permanent effect is to be got. Positive holes are trapped with formation of interstitial Ag^+, which can subsequently participate in the trapping of electrons. Movement of both photoelectrons and Ag^+ is necessary for latent image formation. Stable trapping of an electron by a neutral atomic or molecular group does not occur, but presence of an interstitial Ag^+ can promote trapping. The very shallow trap formed by a surface Ag^+ (e.g. at a kink site) is deepened by presence of an interstitial Ag^+, and an electron can be trapped to form an unstable "pre-image" speck Ag_2^+. If this does not dissociate before arrival of another electron and Ag^+, the stabler neutral "subimage" speck, Ag_2 is formed. This speck can trap an electron in presence of an interstitial Ag^+. An aggregate of > 2 Ag atoms will adsorb a Ag^+ to form a positively charged, stable latent image speck, e.g. Ag_4^+, which can attract electrons but is stabilised by its charge against attack by a positive hole. Ag_2S acts principally as a positive hole trap, but will stabilise Ag atoms formed on the surface against diffusion into the interior along internal surfaces and will react with molecular Br to prevent solarisation. In dye sensitisation, energy from the light quantum raises an electron in the dye molecule to a higher level, and the vacancy in the lower level is filled by an electron from a neighbouring halide ion. The whole electron level of the dye molecule is thereby raised, and an electron can pass from the excitation level into the conductance band of the crystal. Reciprocity failure, the Herschel effect, and the Clayden effect are discussed. C.O.C.

Sorption of Optical Sensitisers on Silver Bromide. I— Adsorption

Z. L. Petrushkina

Zhur. Nauch. i Prikład. Fot. i Kinematograf, 1, 413–418 (1956): *Chem. Abs.*, 51, 14451 (10 Oct. 1957)

Study of the reversibility of adsorption on AgBr of the basic dyes 1:1′-diethyl-6:6′-dimethyl-2:4′-cyanine

iodide, 3:3′:9-triethyl-5:5′-diphenyloxacarbocyanine bromide, 3:3′:9-triethyl-5:5′-dimethoxyoxacarbocyanine bromide and 3:1′-diethyl-5:6-dimethyl-8′-chlorothia-4′-quinocarbocyanine iodide shows that the dyes are completely adsorbed by the AgBr if the concentration of adsorbed dye is $< 0{\cdot}5\text{–}1{\cdot}0\times10^{-4}$ g./g. AgBr in 96% alcohol or $1{\cdot}2\text{–}2{\cdot}4\times10^{-4}$ g./g. AgBr in water. Probably adsorption occurs along the edges of the crystals in aqueous solution and on the crystal faces in alcoholic solution, so that the degree of adsorption is greater from aqueous than from alcoholic solution. C.O.C.

Optical Sensitisation of Photographic Emulsions. VI— Adsorption of Sensitisers on Emulsion Microcrystals of Various Types

B. V. Barbarin and Y. N. Gorokhovskiĭ

Zhur. Nauch. i Priklad. Fot. i Kinematograf, 1 419–424 (1956):

Chem. Abs., 51, 14452 (10 Oct. 1957)

The degree of adsorption of the sensitising dyes Erythrosin (C.I. Acid Red 51), 3:3′-dimethyl-9-ethyl-4:5:4′:5′-dibenzothiacarbocyanine chloride and 1:1′-diethyl-2:2′-cyanine iodide in various types of Ag halide crystals has been studied. The specific adsorption per unit area of crystal surface for crystals of the same size is greatest for those containing AgBr + 3 mole % AgI and least for those containing AgCl. It was greater for fine crystals than for coarse crystals of the same composition and was lessened by both physical and chemical ripening. Probably the adsorption capacity of Ag halide crystals is decreased by interaction with gelatin during ripening and that the lesser sensitisability of coarse-grained emulsions and the difference in contrast of colour-sensitised emulsions in their natural and extended regions of spectral sensitivity are caused by this phenomenon. C.O.C.

Colour Development of Black-and-white Photosensitive Materials

E. Eiler

Papír és Nyomdatechnika, 8, (6), 168–169 (1956): *Hungarian Tech. Abs.*, 9, (3), 89 (1957)

There are six different methods for producing colour contact screens— (1) Coating the silver image with dye. To this group belong all chemical procedures in which the already developed silver image is bleached in an aqueous solution of potassium ferricyanide, potassium citrate, and copper sulphate and then immersed in a dilute solution of a basic dye (e.g. Fuchsin) in acetic acid. (2) Coating the silver images with coloured salts of heavy metals. In this category belong methods in which the metallic silver forming the images is converted into a ferrocyanide or ferricyanide, subsequently forming coloured precipitates from the former by means of a solution of heavy metals. (3) Destruction of dyes. With this procedure the film is impregnated with the corresponding dye, then the silver image is bleached in an aqueous solution of thiourea and citric acid. (4) Image-like tanning of the gelatin layers. With this type the gelatin is not coloured permanently by certain basic dyes. In development with sulphite-free *o*-, *m*-, or *p*-dihydroxybenzene the gelatin is tanned at the patterned parts. There is a considerable dye absorption at these points. (5) Photochemical bleaching of dyes. (6) Chromogenic development, where the developer, being the reducing agent, oxidises itself. Mascolor and Contact Magenta, developers which have recently appeared on the Hungarian market, can also be used for colour correction. The developer Mascolor, by its ability to develop various colours, can also be used for producing mosaic filters. Experiments conducted at the Athenaeum Printing Plant in Budapest proved that considerable progress has been made in the field of automatic colour correction.

C.J.W.H.

Moiré in the Colour Reproduction of Three-colour Autotypy

P. Bayer

Papír és Nyomdatechnika, 8, 6–11 (1956): *Hungarian Tech. Abs.*, 9, (1), 19 (1957)

In autotypy the relative position of the individual dots belonging to two systems of dots printed over each other is a question of chance. They may become arranged concentrically or otherwise. The arrangement of such pairs of dots— selected at random— is repeated within a finite distance, and thus pairs of dots identically arranged can be found in the system. The distance between two identically arranged pairs of dots is called the *phase distance*. By connecting three identically arranged pairs of dots with straight lines, phase areas are obtained, within which the positions of the members of the pairs of dots varies in relation to each other. Any possible arrangement of dots may be found within a phase area, which therefore may be considered an elementary area of the colour field. The colour-resolving power of the autotype depends on the size of this area, which can be calculated on the basis of the screen constant and the inclination of the dot screen systems, and the optimum angle of inclination may be obtained in this way. The sizes of elementary colour areas for various screen systems and angles of inclination are tabulated. The principle of phase areas justifies the computability of the quality of colour reproduction by employing the probability calculus. C.J.W.H.

PATENTS

Photogravure Printing on Cloth

Apponaug Co. *BP* 788,635

The fine details and continuous tone gradations obtained by photogravure printing on paper is obtained on cloth by passing it between a photogravure printing cylinder and a smooth backing. The depth of the depressions on the photogravure cylinder vary from 1 μ to 0·003 in., and the printing paste has viscosity 200–3000 cp. If the cloth has not a smooth surface it must be calendered to give it a temporarily smooth surface. C.O.C.

Pigmented Prints, Impregnations and Coatings on Fibrous Materials

ICI *BP* 787,032

An aqueous composition comprising an epoxide or mixture of epoxides of average functionality >1, a synthetic polymeric rational containing reactive OH or COOH groups, and a basic catalyst is used. Thus 2:2-di[4-(2:3-epoxypropoxy)-phenyl]-propane is made into a smooth emulsion with an aqueous solution of a 9:1 interpolymer of methacrylic acid and β-ethoxyethyl methacrylate in which 80% of the free COOH groups are neutralised with NaOH. To this emulsion is added 2:4:6-tris-(dimethylaminomethyl)phenol and then an aqueous paste of copper phthalocyanine (C.I.74160). Cotton cloth impregnated with the mixture, dried and heated for 1 hr. at 100°c. is coloured fast to washing. C.O.C.

BP 788,664

A pigmented composition comprising polyglyceryl monomethacrylate, a water-soluble precondensate, and an acidic catalyst is used, e.g. polyglyceryl monomethacrylate (6) in water (54) is mixed with Beetle Resin 309 (6) and ammonium thiocyanate (0·5) in water (22) added and finally a 20% paste of copper phthalocyanine (C.I.74160). Spun viscose rayon fabric is impregnated with this mixture and dried and heated for 5 min. at 150°c. The resulting coloration is faster to washing than that obtained in the same way but with the omission of the polyglyceryl monomethacrylate. C.O.C.

Printing on Non-absorbent Surfaces

Wm. Wrigley Jr. Co. *BP* 785,781

Regenerated cellulose film, wax coated paper or the like, is readily printed by means of a porous roller impregnated with coloured wax or other solid material which becomes liquid when hot. The prints do not readily smear or become erased or distorted by rubbing. C.O.C.

Improving the Printability of Polyethylene Films

Celanese Corpn. of America *BP* 787,403

The film is subjected to a corona electrical discharge occurring between a rotatable cylindrical electrode round and in contact with which the film travels with the surface to be treated exposed, and a part-cylindrical electrode concentric with and surrounding the other electrode. C.O.C.

Improving the Printability of Polyethylene Terephthalate Films

ICI *BP* 788,365

Drawn and heat-set polyethylene terephthalate film has its surface subjected to a flame for a period insufficient to cause distortion of the film. This much improves the adhesion of printing ink subsequently applied. C.O.C.

Ensuring Accurate Registration in Multi-colour Printing
Licentia Patent-Verwaltung *BP* 787,390

Pigmented Light-sensitive Composition for Decorating Cellulose, Metal and Vitreous Surfaces
Eastman Kodak Co. *USP* 2,747,997

Pigmented compositions based on polymers having units of structure R·CH:CH·CO— (R = Alk or non-nuclear Ar), e.g. cinnamic esters of poly(vinyl alcohol), are inherently light-sensitive and can be sensitised to increase their speed. They have good stability and are especially suited for use on cellulosic, metal and vitreous surfaces.
C.O.C.

Magenta Colour Couplers
ICI *BP* 786,859

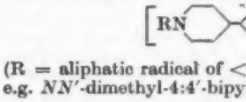
When working the processes described in *BP* 651,059 and 673,091 (J.S.D.C., **67**, 250 (1951) and **68**, 327 (1952)), use as magenta colour couplers of the colourless or almost colourless derivatives obtained by treating pyrazolones with oximes of aromatic aldehydes, masking images of correct intensity are readily obtained by simple treating after development. There is no serious effect on the speed of colour development which is appreciably higher than that of the corresponding styryl dye. Such a colour coupler is obtained by treating 1-(4′-phenoxy-3′-sulpho)-phenyl-3-heptadecyl-5-pyrazolone in alkaline aqueous solution with *p*-di-(ethylcarboxymethyl)aminobenzylidene oxime dissolved in methanol. C.O.C.

Diazo Photographic Reproduction
Eastman Kodak Co. *USP* 2,747,999

A layer of a diffusible diazonium salt is exposed through a negative long enough to decompose the diazonium salt in the exposed areas. It is then pressed against a moist receiving sheet to transfer some of the decomposed diazonium salt by imbibition. The two are then separated and the receiving sheet treated with a coupling component to produce a dye image. This transferring process can be repeated numerous times. C.O.C.

Discharging Filter and Antihalation Dyes in Photographic Films
General Aniline *BP* 788,425

Azo dyes in exposed and developed film are discharged by use of an aqueous alkaline bath containing a strong reducing agent, e.g. sodium hydrosulphite, in presence of a bipyridylium compound of formula—



(R = aliphatic radical of < 5 C or aralkyl; X = anion), e.g. *NN′*-dimethyl-4:4′-bipyridylium chloride, as catalyst.
C.O.C.

Negative Working Diazo Sulphonate Foils
General Aniline *BP* 786,403

Aromatic Diazooxide Sulphonamides as Sensitisers for Lithographic Plates
General Aniline *BP* 787,360

Diazooxides of aromatic sulphonamides in which a terpene radical is attached to the amido N atom, e.g. *N* - dehydroabietyl - 6(5H) - diazo - 5,(6H) - oxo - 1 - naphthalenesulphonamide are excellent sensitisers for lithographic plates and have the great advantage of being readily soluble in common organic solvents.
C.O.C.

Dyeing and Printing Cellulose Acetate, Nylon, Polyester Fibres or Films, and Cyanoethylated Cellulose (III p. 190)

Structure of Sensitising Dyes adsorbed on Silver Halide Crystals (IV p. 194)

Oxidation Bases for Printing (IV p. 201)

Yellow Nonfluorescent Schiff's Bases (IV p. 201)

Inks for Printing on or Dyeing Plasticised Polyvinyl Acetal Sheeting (V p. 203)

Synthetic Resinous Binders for Pigment Padding and Printing Compositions (VIII p. 209)

Electrolytic Recording Papers (XI p. 214)

X—SIZING AND FINISHING

Capillary Drying of Textiles
K. Messik, T. Bonkáló, and K. Szabó
Magyar Textiltechnika, (3), 111–114 (1956): *Hungarian Tech. Abs.*, **9**, (1), 20 (1957)

In order to remove the water remaining in the capillaries of cloths after the conventional mechanical squeezing, forces similar to those which bind it, i.e. the capillary action of dry capillary systems, must be used. In textile-finishing mills dry piece goods which are to be subsequently wet-treated are employed for this purpose. If the wet cloth and the dry cloth are brought into close contact with each other in suitable equipment, the capillary forces draw water into the dry cloth. After a time equilibrium is reached and the water is evenly distributed between the layers. The initial water content of a cloth can be decreased by 45% by this method, and thus the energy required for the drying also decreases by 45%. Experiments carried out in the laboratory and in a finishing mill proved that most goods made of any kind of fibre (cotton, viscose, rayon, staple fibres, wool), whether dyed or undyed, can be dried by capillary forces. C.J.W.H.

Acetylation of Cotton with Acetic Anhydride Vapour
I— Acetylation with Sulphuric or Perchloric Acid Catalyst
I. Sakurada and Y. Sakaguchi
Sen-i-Gakkaisha, **13**, 13–16 (1957)

II— Acetylation with Salt Catalysts and the Properties of Acetylated Fibres
Ibid., 67–72

III— Acetylation of Cotton and Ramie Yarns
I. Sakurada, Y. Sakaguchi, and H. Yamaguchi
Ibid., 72–5: *Chem. Abs.*, **51**, 15116 (10 Oct. 1957)

I— Blended cotton immersed 10 min. in N-H_2SO_4 or N-$HClO_4$, excess acid squeezed out, and exposed to acetic anhydride vapour for 2·5–18·0 hr. at 30–60°C. was acetylated 50–93%. The moisture content could be diminished to about 10% by pretreating with lower alcohols or esters without impeding the reaction. The acetylation velocity was slower than that of rayon acetylated under the same conditions.

II— $ZnSO_4$ was as good a catalyst as H_2SO_4, but $ZnCl_2$ is not as good unless in high concentration, which is apt to cause fibre damage. From the re-acetylation velocity, water absorption and solubility in $CHCl_3$ and $(CH_3)_2CO$, H_2SO_4 and $ZnSO_4$ apparently catalyse the reaction similarly, while ZnO_2 seems to activate the amorphous region selectively.

III— Cotton and ramie yarns using H_2SO_4 or $ZnSO_4$ as catalyst were acetylated as rapidly and to the same extent irrespective of the yarn count. Raw cotton yarn acetylates slightly slower than blended yarn. The acetylation did not affect the dyeing properties or tensile strength, but shrank the fibres (up to 20%) with the higher acetylation. Shrinkage could be avoided by acetylation under tension. Ramie yarn shrinks less than cotton.
C.O.C.

Aftermercerisation of Cotton Fabrics treated with Methylolmelamine Resin
L. W. Mazzeno, R. M. Reinhardt, A. R. Markezich, and J. D. Reid
Amer. Dyestuff Rep., **46**, 719–724 (7 Oct. 1957)

The beneficial effects of mercerising cotton before resin treatment are well known. In this paper it is shown that mercerisation after resin treatment improves tear strength and abrasion resistance. The optimum treatment appears to be with 20% NaOH at 25°C. for 5 min.: this gives the greatest improvement in tear strength and abrasion resistance with the least loss of wrinkle-resistant properties. If more than 10·5% resin is applied, the alkali is unable to penetrate to cause mercerisation. Aftermercerisation has a much greater effect on the abrasion resistance than premercerisation. Preliminary experiments on refractive indices and moisture regain of treated fibres and X-ray diffractometer experiments give evidence of the degree of mercerisation. P.T.S.

Impregnation of Yarns for Fishing Nets
J. Zaucha
Technika i Gospodarka Morska, (5), 135–136 (1956): *Polish Tech. Abs.*, (23), 137 (1957)

(1) Cotton yarn was tanned, fixed with copper and

chromium compounds, and tarred; after 3 months' immersion in water it lost 30% of its resistance. (2) A second yarn was preserved by means of a sulphur dye with an admixture of copper, and lost 50% of its resistance after 50 days' immersion. Non-impregnated yarn lost in the same time 90% of its resistance. Impregnation costs under method (2) do not exceed 3% of the cost of the net.
C.J.W.H.

Techniques and Economic Importance of the Crease-resisting of Viscose Rayon
E. Pieper
Reyon, Zellwolle, Chemiefassern, (4), 277–279 (1956): *Tint. ind.*, (30), 349–371 (Aug. 1957)

A review of the factors influencing the recovery from creasing and the processes available is made. The export of viscose rayon textiles from Germany increased nine times from 1950 to 1954 and since a large proportion of these were crease-resisted the Güteverband Hochveredelt was formed. Minimum requirements are— at least 110° after 60 min., water imbibition reduced by at least 40% up to 65%; wet-ironing warp or weft shrinkage $\not>$ 1%. The work of the Dyeing and Finishing Subcommittee of the International Rayon Synthetic Fibres Committee showed that the slight increase in crease recovery at resin loadings of $>$ 12–14% is more than outweighed by the increased rapidity of wear.
S.R.C.

Treatment of Silk Fibres with Diazomethane. I— Synthesis and Selection of the Solvent for Diazomethane
T. Kuwamura, Y. Nakamura, and M. Negishi
J. Soc. Textile Cellulose Ind. Japan, **13**, 547–552 (Aug. 1957)

The practical methylation of silk to improve its resistance to light may be carried out with an acetone solution of diazomethane, which may be synthesised by the method of Boer and Backer (*Rec. Trav. chim.*, **73**, 229 (1954)).
C.J.W.H.

Angora Rabbit Fibres. XVII— Ageing Effect on the Mechanical Properties of Carrotted Fibres
S. Ikeda and S. Okajima
J. Soc. Textile Cellulose Ind. Japan, **13**, 541–546 (Aug. 1957)

Angora rabbit fibres were immersed in a solution containing $Hg(NO_4)_2$ (1·8%) and HNO_3 (3·6%) at 30°c. for 30 min. After being squeezed, they were dried at 95°c. for 30 min., and aged for 3–12 months at 35±1°c., during which time the change in their mechanical properties was traced and the following results were obtained— (1) The mechanical properties changed when the ageing period became greater than 3 months, but the change after 3–12 months was statistically negligible. (2) When the carrotted fibres were aged after being washed, no effect of ageing was observed.
C.J.W.H.

Impregnation for Water Repellency and its Combination with Synthetic-resin Finishing
H. Ruile
Melliand Textilber., **38**, 313–319 (March 1957): *Amer. Dyestuff Rep.*, **46**, 947–952 and 977 (16 Dec. 1957)

PATENTS

Reducing the Water-imbibition of Regenerated Cellulose
Courtaulds *BP* 786,383

Impregnation with aqueous propiolic acid or with aqueous propargyl alcohol and a mercuric chloride catalyst and then baking at 100–150°c. much reduces the water-imbibition of regenerated cellulose. Thus regenerated cellulose rayon impregnated with a 3% aqueous solution of propiolic acid, dried and baked at 140°c. for 1 hr., had a water imbibition of 46% compared with 96% for the untreated rayon.
C.O.C.

Treating Cotton Sliver with Caustic Alkali Solutions
U.S. Secretary of Agriculture *USP* 2,751,278

By controlling the amount of lye which comes into contact with the sliver level results can be obtained and the sliver can be continuously processed using ordinary apparatus. The sliver is treated with enough lye to wet all the fibres but insufficient to allow it to entrain enough liquid as to cause it to break as it is withdrawn from the mercerising bath. The wet sliver can be immediately washed or, where there is another component in the bath, it may be heated to cause the necessary reaction. Thus cotton sliver coming from the card is impregnated with mercerising lye, passed through squeeze rolls, passed several times through water and squeeze rolls and dried. Yarn produced from it had the characteristics of mercerised cotton yarn. In another example cotton sliver was impregnated with caustic lye containing 2-aminoethylsulphuric acid, squeezed, dried at 110°c. for this to cause the 2-aminoethylsulphonic acid to react with the cellulose, washed and dried. Yarn spun from it had the properties of aminised cotton yarn.
C.O.C.

Increasing the Water-absorption of Polyamide Fibres
FBy *BP* 788,688

The fibres are treated with an aqueous or aqueous alcoholic colloidal solution or emulsion of a nitrogen-methoxy methyl polyamide in presence of a water-soluble linear polyester obtained from a dihydric alcohol and a dibasic acid and then heated to $>$ 100°c.
C.O.C.

Sizing and Polishing of Yarns
Wm. Ayrton & Co. *BP* 786,482

The yarn is sized and then treated with a rotary brush. Guides lead the yarn in a closed polygonal path at least once round the brush rod so that a number of spans of yarn between the guides are treated by the brush. Means are also provided to prevent the feedback, at least between consecutive convolutions, of yarn tension caused by the brushing.
C.O.C.

Lubrication of Sewing Threads
Dow Corning Corpn. *BP* 788,143

Sewing threads made from regenerated cellulose or a cellulose derivative are impregnated with a liquid organopolysiloxane whose organic radicals are monovalent radicals attached to the Si atoms through Si–C linkages. The process is particularly applicable to threads of ethyl cellulose.
C.O.C.

Phenylaminoalkylated Cellulosic Textiles and their Chemical Modification including Colouring
U.S. Secretary of Agriculture *USP* 2,750,249

Cellulosic textiles in which alcohol H atoms have been replaced by aminoalkyl radicals, e.g. by the process of *USP* 2,459,222, when treated with a halogen and nitro-substituted aromatic hydrocarbon in presence of dil. aq. alkali yield products in which alcoholic H atoms have been replaced by N-(nitro acyl)aminoalkyl radicals. They retain affinity for acid dyes and when treated with an aqueous reducing agent yield *N*-(amino acyl)aminoalkylated cellulosic textiles which can be diazotised and coupled. Thus amino alkylated cotton cloth produced according to *USP* 2,459,222 was treated with 1-chloro-2:4-dinitrobenzene in presence of aqueous caustic soda at 70–90%c. The product had physical properties similar to those of the original amino alkylated cloth. It was then treated with $Na_2S_2O_4$, diazotised and coupled with 1-naphthol-5-sulphuric acid to yield a dark red-brown cloth.
C.O.C.

Durable Stiffened Finishes on Synthetic Fibre or Thermoplastic Cellulose Fabrics
British Industrial Plastics *BP* 787,674

Fabric made from nylon, Terylene, acetate rayon or the like is impregnated with an aqueous solution containing (*a*) a water-soluble lower alkyl ether of a methylol urea (urea:HCH::1:5 to 1:2) in which $\not<$ 75% of the methylol groups are etherified and (*b*) a curing agent, dried and baked. Thus 30 denier nylon net is padded with a 30% solution of methylolureas of urea-formaldehyde ratio 1:1·9 and 85% methylated and 1·5% thiocyanate, dried and baked for 2 min. at 240°c. This yielded a stiff finish fast to wash and dry cleaning, free from "chalking" and the inflammability of the fabric was unaffected.
C.O.C.

Flame-resistant Finish of High Fastness to Leaching
British Jute Trade Research Assocn. *BP* 785,610

The materials are treated with an aqueous dispersion containing antimony orthophosphate, a chlorine-containing vinyl thermoplastic resin, and a stabilising agent, and then cured. Thus jute cloth is impregnated with an aqueous dispersion containing an internally modified chlorine-containing vinyl resin, $SbPO_4$ and sodium carboxymethyl cellulose and dried at normal drying temperature. This yields a fabric which is very resistant to flaming and to smouldering.
C.O.C.

Rotproofing with Copper Formate
National Cylinder Gas Co. *USP* 2,749,256
The cellulose is impregnated with copper formate and then heated to $< 100°C$. This yields a copper-cellulose complex the copper of which is not removed by leaching with 4% aq. ammonia for 24 hr. Similarly the cellulose of the complex is not affected by cupriethylene diamine, cuprammonium, mineral acid or caustic alkali. C.O.C.

Continuous Decatising
G. Sperotto *BP* 786,833
In a continuous decatising machine better results are obtained if instead of using only a single cylinder, the fabric is treated on several cylinders in succession, the quality and temperature of the steam used in each cylinder being raised from one cylinder to the next in accordance with requirements. C.O.C.

Water-repellent Finish
Wacker Chemie *USP* 2,789,956
When applying silicone finishes to textiles better and more durable water-repellency is obtained and the temperature of baking can be lowered if the textiles are treated before, during or after the application of the silicone with an aqueous solution of a zirconium compound having affinity for the fibres, e.g. zirconyl chloride, acetate or nitrate. C.O.C.

Treating Polyester Fibres with Alkalis
FH *BP* 786,153
When treating polyester fibres with alkalis addition of a glycol and/or a polyglycol or an ester or ether thereof speeds up the reaction and enables lower temperatures and lower concentrations of alkali to be used. Thus Terylene fabric is treated for 90 min. at 98–100°c. in an aqueous bath containing NaOH (25 g./litre) and a polyglycol of average mol.wt. 4000 (25 g./litre). The loss in weight of the fabric is 5% less than that if NaOH is used alone, yet the handle of the treated material is practically as soft in both cases. C.O.C.

Compressive Shrinking
Cluett, Peabody & Co. *BP* 785,139
Means are provided during the compressive shrinking of fibres to indicate automatically the ratio between the feed and delivery speeds. C.O.C.

Increasing the Abrasion-resistance of Textiles by Treatment with Werner Type Complexes
DuP *BP* 785,784
Fibres in general when treated with solutions or dispersions of unpolymerised Werner type complexes which have been brought to pH 4–7 by adding a nitrogen base, have their resistance to abrasion much improved. The treatment is particularly applicable to glass fibres which are not only rendered abrasion resistant but also capable of forming strong bonds with polyester and similar resins, these bonds being unaffected on prolonged exposure to water or high humidities. C.O.C.

Soil-resistant Pile Fabric
Mohasco Industries *BP* 785,673
The visible portion of the pile is treated so that its surface is coated with discrete fine particles of a non-film-forming polymer of vinyl chloride or acetate or styrene or a vinyl chloride-vinylidene chloride or styrene-butadiene copolymer. Thus the pile may be sprayed with or treated by an applicator roller with a dilute solution of one of these resins whose particles do not coalesce to form a film when the fabric is dried. C.O.C.

Reducing the Tendency of Textiles to Pick Up Dirt
R. White *BP* 788,020
After being washed the textiles are given a coating of partly neutralised stearic acid. C.O.C.

Permanently Embossed Elastic Webbing
Moore Fabrics *USP* 2,748,447
Webbing is woven with a warp of elastic threads under tension and so that the warp is completely covered by the weft of non-elastic yarn. The webbing is then relaxed, sized and dried in absence of tension. It is then passed through a bath of coating material, dried and then embossed. C.O.C.

Metallised Fabric
A. F. Schramm *USP* 2,748,019
A permeable sheet is coated with a dispersion of a solid binder. Metal flake in an uncovered form, i.e. not suspended in a plastic or like solution, is then applied, the liquid dried off from the dispersion, the metal flake is pressed against the plastic binder, and finally the binder is hardened. C.O.C.

Reducing the Tendency of Synthetic Fibre Fabrics to Pill
DuP *BP* 786,868
The fabric is gently treated with a rapidly revolving brush so that there is heel to toe contact between the bristles and the fabric surface. This effects random flattening of the fibres in the exposed crowns of the yarns of the fabric. The flattened fibres are then compressed against adjacent fibres so as to lock them with the body of the fabric, this being preferably achieved by shrinking, e.g. in an overfeed tenter. C.O.C.

Improving the Soil Resistance of Fabrics
Alexander Smith *BP* 787,476
The exposed surface of the fabric is coated with discrete, preformed aluminium phosphate of average particle size > 70 mμ. This renders the fabric less liable to pick up and retain dirt. C.O.C.

Non-slip Fabric
Riegel Textile Corpn. *BP* 787,798
One or both surfaces of the fabric is spotted with dots of plasticiser resin which is soft to the touch and somewhat tacky and compressible, e.g. a cotton fabric is spotted with a mixture of equal weights of vinylchloride resin and a dialkyl phthalate. C.O.C.

Artificial Fibre Sheeting as Paper Substitute
M. Noberasco *BP* 787,769
A nylon fabric has its weft and warp fused together by heat and is then coated on both sides with a synthetic resin or cellulose derivative. At least one side is then given a further coating of a pigmented synthetic resin or cellulose derivative. The product is very light and paper-like, can be printed on, is resistant to water and acid, non-inflammable and of very high tensile strength. C.O.C.

Flexible Coated Sheeting
ICI *BP* 788,547
Apparatus in which cloth, etc. is coated in stripes. The width of the stripes may be altered quite simply. The stripes are separated by uncoated cloth, the width of these uncoated portions also being readily varied or made exceedingly fine. C.O.C.

Light-reflecting Flexible Sheeting
James Halstead *BP* 788,782
A woven backing is coated on one face with a smooth layer of plastic material. On this layer is superposed a mirror-like layer of light-reflecting material and then a second layer of transparent plastic. A layer of discrete reflex-reflective particles, e.g. minute balls of glass, are partially embedded in the upper surface of the second layer of plastic. Finally a third layer of clear plastic is applied to enclose these particles and impart a smooth surface to the finished product. C.O.C.

Application of Fluid Beds to Textile Processing (I p. 188)
Chemical Modifications of Natural Fibres (VI p. 204)
Pigmented Prints, Impregnations and Coatings on Fibrous Materials (IX p. 210)
Formaldehyde Evolution from Textiles (XIV p. 220)
Silicone Resins in Finishing (XIV p. 220)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

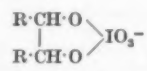
Molecular Weight of Native Celluloses
T. E. Timell
Svensk Papperstidning, 60, 836–842 (30 Nov. 1957)
Investigation of the molecular weight of the cellulose component, from twenty-two different cellulosic materials is described, and it is concluded that native cellulose possesses the same average molecular weight, irrespective of origin. The D.P. values obtained were considerably higher than those reported previously for the same materials, and possible reasons for this difference are discussed. G.S.B.

Effect of γ-Radiation on Cellulose
R. E. Glegg and Z. I. Kertesz
J. Polymer Sci., **26**, 289–297 (Dec. 1957)
Cotton and wood cellulose were irradiated with γ-rays, and the degradation was estimated from viscosities in cupriethylenediamine solution. The presence of water had no significant effect on radiation-induced degradation. The radiation threshold dosage for isolated celluloses appears to be in the range $28{\cdot}4–81{\cdot}2 \times 10^3$ rontgens. W.R.M.

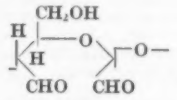
Degradation of Cellulose by Aqueous Sodium Hydroxide at 170°C.
W. M. Corbett and G. N. Richards
Svensk Papperstidning, **60**, 791–794 (15 Nov. 1957)
The major soluble products from the degradation of cotton cellulose by 0·5 N-NaOH at about 170°C. have been examined and their yields compared with those obtained from hydrocellulose by the same reagent at 100°C. The products arise from the progressive stepwise alkaline degradation of hydrocelluloses produced by chain scission of the original cellulose molecules, the scission resulting from the action of the aqueous alkali alone and not from oxidation by traces of atmospheric oxygen or ferric ions. G.S.B.

Destruction of Cellulose dissolved in Mercerising Liquor
O. Franzon and O. Samuelson
Svensk Papperstidning, **60**, 720–724 (15 Oct. 1957)
Bleached sulphite pulp and hydrocellulose prepared from purified cotton were mercerised in the investigation, and after separation of the undissolved cellulose, the mercerising liquor was kept at different temperatures for different periods of time. The amount of precipitable cellulose in the liquor decreases rapidly even at moderate temp., e.g. at 40°C. Dissolved cellulose containing carbonyl end-groups, is easily attacked, whereas cellulose molecules containing carboxyl end-groups are much more stable. G.S.B.

Mechanism of the Oxidation of Cellulose by Periodate
T. P. Nevell
J. Textile Inst., **48**, T 484–T 494 (Dec. 1957)
The mechanism of cellulose oxidation (from the effect of variations in temperature, pH, salt, and periodate concentrations) is thought to be analogous to the oxidation of glycols by periodate ions, where an intermediate complex is involved—



which decomposes slowly to give $2R{\cdot}CHO + IO_3^-$. The cellulose analogue—



is sensitive to alkali, and will undergo scission to give soluble products and new end-groups. P.T.S.

Rapid Method of Fractionation of Viscose Rayon and Cellulose of Low Degree of Polymerisation
T. Skwarski and B. Gawronsko
Zesz. Nauk. Politech. Lodz., No. 15 (*Chemia* 5), 103–106 (1957)
O. Fuchs's method for the fractionation of polymers was used for the fractionation of cellulose of low D.P. and viscose rayon. The method is very rapid and gives reproducible results. T.Z.W.

Viscosity Measurements on Dilute Cellulose Xanthate Solutions
L. Oldsberg and O. Samuelson
Svensk Papperstidning, **60**, 745–750 (31 Oct. 1957)
The results of viscosity measurements on cellulose xanthate solutions obtained by ion exchange of dilute solutions of viscose are discussed, and it is shown that dilute solutions of cellulose xanthate behave like other polyelectrolytes and also exhibit great similarities to certain other cellulose derivatives. No indications of a micellar structure were obtained. G.S.B.

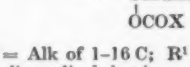
Xanthate Groups in Partly Substituted Cellulose Xanthate
E. P. Swan and C. B. Purves
Canadian J. Chem., **35**, 1522–1533 (Dec. 1957)
Cellulose sodium xanthates of degree of substitution 0·4–0·6 were methylated to *S*-methyl esters, which were then completely acetylated. Dexanthation with aqueous chlorine dioxide removed nearly all the *S*-methylxanthate groups. The original xanthate groups were presumed to be represented on the resulting acetate as unsubstituted hydroxyl groups, and these were located by standard methods. Xanthate groups appeared to occupy the third and sixth but not the second position in cellulose. 53–61% were in the sixth or primary position. The results are to be regarded as of a preliminary nature, as technical difficulties reduced their reliability. W.R.M.

Structure of Cellulose Triacetate
W. J. Dulmage
J. Polymer Sci., **26**, 277–288 (Dec. 1957)
An X-ray diffraction study is made of cellulose triacetate II using small films of highly crystalline triacetate with good fibrous orientation. The unit cell is determined, and it is found that the triacetate II has four cellobiose acetate residues in a pseudo-orthorhombic cell. Pairs of residues are related by twofold screw axes in the fibre axis direction. The structure is discussed, and a second, very similar model considered. W.R.M.

Structure of Carboxymethylcellulose and its Derivatives
O. M. Klimova and M. G. Kristalinskaya
J. Appl. Chem. U.S.S.R., **30**, 1421–1424 (Sept. 1957)
Carboxymethylcellulose, prepared by the action of chloroacetic acid on cellulose, was subjected to acetylation and benzylation. It was found that introduction into cellulose of radicals having free carboxyl end-groups decreases its ability to form simple and complex ethers, but does not decrease the reactivity of its hydroxyl groups. Preferential formation of ethers with the primary alcoholic groups was observed. T.Z.W.

PATENTS

Thiourethanes of Cellulose Esters
American Viscose Corpn. *USP* 2,748,109
Products of formula—



(X = Alk of 1–16 C; R^1 and R^2 = H, Alk of 1–2 C, an alicylic radical having a 4- to 6-membered carbocyclic ring, a 5- or 6-membered heterocyclic ring or Ar) are produced by treating the selected cellulose thiourethane with the appropriate organic acid. They have softening temperatures of 200–260°C. and are readily extruded or moulded. They are readily dyed with acid dyes. *USP* 2,748,110

The acid used is an acrylic acid of formula $CH_2{:}CHX$ (X = cyano or $CONY^1Y^2$ (Y^1 and Y^2 = H, Alk of 1–3 C). Cyanoethyl, amidoethyl or Alk-subst. amidoethyl ethers being formed by the 1:4-addition of the acrylic acid derivative to the cellulose thiourethane. C.O.C.

Adherent Synthetic Resin Coatings on Pergamyn and Parchment Papers
Chemische Werke Hüls *BP* 787,482
The incorporation of 5% of shellac in synthetic resin coatings achieves moisture resistant adherence to parchment type papers. G.S.B.

Electrolytic Recording Papers
Air Associates *BP* 786,690
Paper or other suitable carrier is impregnated with a buffered solution of pyrogallol, catechol, resorcinol, hydroquinone, benzenepentol, benzenetetrol, phloroglucinol, hexahydroxybenzene, *o*-hydroxyquinone, or α- or β-naphthol, an activating electrolyte, e.g. a water-soluble alkali metal salt, and a lake-forming metal complex, preferably a ferric complex, e.g. ferric nitrate and citric acid. C.O.C.

Silicone Treatment of Paper for Thermographic Reproduction
A. B. Dick Co. *USP* 2,749,253
Better copies with less burn-out are obtained if the base paper for the copy sheet is treated before, during or after

application of the sensitising material, with an organo-silicon compound. C.O.C.

Monoazo Compounds as Absorbents for Ultraviolet Radiation (III p. 191)

Lead Chrome Pigments for Colouring Cellulose Acetate (IV p. 202)

Artificial Fibre Sheeting as Paper Substitute (X p. 213)

Thiourethanes of Cellulose Esters (XI p. 214)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Chemical Studies on the Liming of Animal Skin. VII—Effects of Organic Nitrogen Compounds in Accelerating the Unhairing of Animal Skin by Lime Liquor—Part 2

H. Toyoda and A. Futami

Rept. Govt. Chem. Ind. Research Inst. Tokyo, **52**, 321–327 (xxxix) (Sept. 1957)

The accelerating actions of various organic nitrogen compounds on the unhairing of animal skins in lime solutions have been studied by measuring the loads required for unhairing. Among the compounds tested, ethanolamine, hydroxylamine, *N*-methylhydroxylamine, hydrazine, guanidine, aminoguanidine, and biguanide accelerate unhairing, and *S*-ethylthiourea has a great dissolving action on keratin. The others are ineffective or retard unhairing. The activity of the organic nitrogen compounds is closely related to their chemical structures and is not always parallel to the strengths of the compounds as bases. Generally speaking, the effective compounds have the following structures: $R{\cdot}NH_2$, R_2NH, $R{\cdot}NHOH$, $R{\cdot}NH{\cdot}NH_2$, $R{\cdot}C(:NH){\cdot}NH_2$. But the activity is markedly influenced by the structures of residues R and R′. When R and R′ are hydrogen atoms, amino groups, or alkyl groups, the compounds are generally effective. C.J.W.H.

Artificial Polyamide Coating (Surface Finish) on Chrome-, Vegetable-, and Sulphonyl-chloride-tanned Splits. I and II

W. Grzywinski

Przeglad Skórzany, (6) and (12), *Biul. Labor. Kolor.*, 1–4 and 5–8), (1956): *Polish Tech. Abs.*, (27), 151–153 (1957)

I—Attempts were made to improve splits by applying a polyamide coating (surface finish). Since the Polish polycaprolactam (Steelon) in calcium chloride saturated ethanol produced coatings which came off easily and were brittle, further attempts entailed a modification of the substance, viz., *N*-alkoxymethylpolycaprolactam. A mixture of 95% ethanol with butyl or amyl alcohol was used as solvent. The adhesive properties of the coating thus produced were fairly good, particularly when 5% of calcium chloride per weight of Steelon was added. The Steelon coating obtained admits of an unlimited range of colours. Using pigments and soluble dyes, virtually any desired shade of a colour can be obtained.

II—The coating is applied to wet splits glued on the glass plates or other non-water-absorbing resins with the aid of starch glue. Basically, two kinds of solutions are used for coating—(1) 10% ethoxybutoxymethyl-Steelon, solution, with imine group substitution of about 42% and (2) 10% ethoxymethyl-Steelon solution, with imine group substitution of 28%. The solution is applied with brushes having relatively long and soft hair. The first coating consists of liquid, non-gelling solution of highly substituted Steelon acidified with 1% of formic acid (65%) and warmed to about 35–40°c. Immediately after the first layer has set, usually after 10–15 min., a second and possibly a third layer is applied using high- and low-substituted Steelon solution mixed in a proportion of 1 : 1. During drying, the maximum temperature ought not to be more than 45°c. After drying comes the process of kneading, rolling, and pressing. The surface obtained very much resembles the natural grain side, but is less soft and pliable (owing to absence of a suitable plasticiser) and is less permeable to air. C.J.W.H.

Optical Rotation and Infrared Spectra of some Polypeptide and Protein Films

A. Elliott, W. E. Hanby, and B. R. Malcolm

Nature, **180**, 1340–1341 (14 Dec. 1957)

The dispersion of optical rotation has been used to study configurations in solid films. Films of poly-L-alanine show the anomalous dispersion of the α-helix. Results with films of water-soluble silk fibroin, lysozyme, and the sodium salt of poly-L-glutamic acid show the absence, or at least low concentration, of the helical form. The silk films show a carbonyl group at 1660 cm.$^{-1}$, but the absence of a band at 1630 cm.$^{-1}$ shows that they are not in the extended β form. It is suggested that a carbonyl band at about 1660 cm.$^{-1}$ may be observed not only with the α-helix and collagen folds but also in what seems to be a disordered state. W.R.M.

Fixation of Casein Coatings by Gaseous Formaldehyde

I. Mustea

Ind. usoară (*Bucharest*), **4**, 126–131 (1957): *Chem. Abs.*, **51**, 17216 (20 Nov. 1957)

Gaseous formaldehyde is now being used in Roumania on a commercial scale for fixing casein coatings on leather. The physical and mechanical properties of the treated leather are much better than when aqueous solutions of formaldehyde are used. C.O.C.

PATENTS

Tanning with Double Silicates of Zirconium and Alkali Metals

Rohm & Haas *BP* 786,769

The skins are treated in an acid aqueous dispersion at $\geq$ 35°c. of a double silicate of Zr and an alkali metal M, the ratio $SiO_2 : ZrO_2$ being $\geq$ 1·5 : 1·0 and of $SiO_2 : M_2O$ $\geq$ 3 : 1, e.g. Na_2ZrSiO_5. C.O.C.

Removing Chromium Soaps from the Wool or Hair of Chrome-tanned Pelts

Boehme Fettchemie *BP* 787,138

Chromium soaps are readily removed by treatment with an aqueous solution of complex-forming compounds containing carboxyl, hydroxyl or phosphine acid groups and a lipophilic residue, e.g. phosphoric acid ester of an aliphatic (C_{12}–C_{18}) alcohol alkoxylated with 8 mol. of ethylene oxide. C.O.C.

Waterproofing of Leather

ICI *BP* 788,741

The leather is treated in presence of a water-soluble zirconium salt with an aqueous emulsion of an organo-polysiloxane. The emulsion contains a water-soluble soap. Finally the leather is treated with a water-soluble aluminium salt. This yields a waterproof leather of very good appearance. C.O.C.

Fat-liquoring of Chrome-tanned Hides

Boehme Fettchemie *BP* 788,657

Addition of a masking agent, e.g., oil-soluble fast-oil esters or fast-oil amides of carboxylic acids containing 3 or more carboxyl groups, to the fat liquor has the same effect as their addition during tanning or neutralisation, i.e., a full leather with firmly applied grain and grain form is obtained. C.O.C.

XIII—RUBBER; RESINS; PLASTICS

Large Periods in Polyethylene: Origin of Low-angle X-Ray Scattering

A. Keller and A. O'Connor

Nature, **180**, 1289–1290 (7 Dec. 1957)

Most crystalline polymers show discontinuous X-ray diffraction effects at small angles indicative of a structural discontinuity of about 100 A. Wide-angle studies of polyethylene indicate a periodicity of 120 A., corresponding to planes parallel to the surface. Discontinuous low-angle scattering effects are produced by larger structures within single crystals. This is interpreted as resulting from regularity of chain folding, the low-angle diffraction recording the periodicity of the folding. Studies of extruded polythene and 6,6-nylon suggest that, when single crystals aggregate to form spherulites, the original layering become parallel to the radius of the spherulite. W.R.M.

Fibrillar Structure of Spherulites in Polyhexamethyleneadipamide

F. Khoury

J. Polymer Sci., **26**, 375–379 (Dec. 1957)

An etching technique is used to show the fibrillar structure and growth of spherulites, in unpolarised light, in films of 6,6-nylon crystallised from the melt between 240° and 255°C. W.R.M.

Effect of Hydrogen Chloride on the Infrared Spectrum of Nylon

P. Larose

Canadian J. Chem., **35**, 1239–1247 (Nov. 1957)

The infrared spectra of films of Zytel (40 : 30 : 30 copolymer of 6-, 6,6-, and 6,10-nylons) cast from alcohol soln. have been examined after exposure to HCl gas, DCl, and D_2O and after casting from soln. in CH_3OD, as well as in the untreated state. Changes in the bands for the –CO·NH– group show interaction of this group with HCl (and DCl). The results indicate in particular that the two –NH– bands at 3300 cm.$^{-1}$ and 3030 cm.$^{-1}$ (for the untreated film) are associated with –NH– groups in different conditions. The general effect of HCl is best explained in terms of polar interaction with doubly charged amide groups—

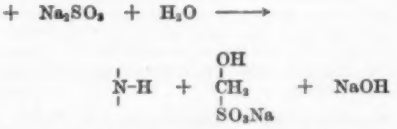
rather than hydrogen bonding or salt formation with uncharged amide groups. A.J.

Preparation of *N*-Methoxymethyl and *N*-Hydroxymethyl Derivatives of Caprolactam and Determination of their Viscosity

T. Skwarski

Zesz. Nauk. Politech. Lodz., No. 15 (*Chemia* 5), 29–64 (1957)

By the action of paraformaldehyde in CH_3OH on the polymer produced by the hydrolytic polymerisation of caprolactam dissolved in conc. formic acid, *N*-methoxymethyl derivatives of the polymer are produced together with small quantities of *N*-hydroxymethyl compd. The degree of substitution depends on the quantity of paraformaldehyde used and can be determined by potentiometric titration of the NaOH produced on treatment with Na_2SO_3—



The derivatives are soluble in the mixture of CH_3OH and $CHCl_3$ and have higher m.p. than the polymer. The soln. of the derivatives of the polyamide in the mixture of methanol and chloroform, and *m*-cresol have higher viscosity, which is due to the presence of the side-chains. Conc. H_2SO_4 and H·COOH cause hydrolysis of the side-chains together with the formation of cross-linkages. T.Z.W.

Coloration of Plastics by Irradiation

S. H. Pinner and A. J. Swallow

Plastics, **22**, 194–5, 268–270 (1957)

Many coloured plastics have their colour changed if they are irradiated with fast electrons from a 2-m.e.v. 0·5-kw. van de Graaf accelerator. Compositions based on poly(vinyl chloride) are especially responsive and can be printed by this means. Transparent CH_2:CCH_3·$COOCH_3$ polymer whose colour has been changed by this means returns to its original colour on being heated or exposed to oxygen. C.O.C.

PATENTS

White or Lightly-coloured Butyl Rubber Compositions of Improved Weathering and Discolouring Resistance

Esso Research & Engineering Co. *BP* 786,016

Combining butyl rubber with 10–150% of MgO (C.I. 77711) or CaO, 10–150% of TiO_2 (C.I. Pigment White 6) and 3–50% of ZnO (C.I. Pigment White 4) (all on the weight of the rubber) enables light colour vulcanisates to be obtained which resist weathering and discoloration and neither craze nor crack. When CaO is used, the surface powdering phenomenon renders the vulcanisates self-cleaning. C.O.C.

Slip-finish Flock-coated Rubber Article

United States Rubber Co. *BP* 787,417

A thick strongly bonded flock coating having a slip finish, i.e. a lower coefficient of friction between the coating and human skin than between rubber and skin, is produced by coating with a mixture of flock and rubber latex and then halogenating the coating. Finally the coating is treated to reduce tackiness and then raised to expose the fibres. C.O.C.

Gelling Hydroxyl Polymers

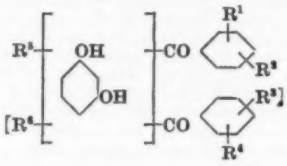
DuP *BP* 786,346

The water-sensitivity of a hydroxyl polymer is reduced by treating it with a water-soluble, amorphous organotitanium compound obtained by condensing 1 mol. of a compound of formula $Ti(OAlk)_4$ (Alk of 1–8 C) with 0·5–4·0 mol. of a saturated aliphatic hydroxy mono-, di- or tri-carboxylic acid of 2–6 C having a hydroxyl group in *α*-position to any carboxylic radical, e.g. the product obtained by condensing lactic acid with tetra*iso*propyl titanate as described in *BP* 757,190. The gelled polymer is resistant to prolonged treatment in water at 25–100°C. C.O.C.

Rendering Thermoplastic Materials Faster to Light

Dow Chemical Co. *BP* 786,144

Addition of 0·1–10·0% of a compound of formula—



(R^1–R^5 = same or different, H, Cl, Br, F, Alk of 1–8 C, $COOR^7$ (R^7 = Alk of 1–8 C, phenyl, monochloro- (or bromo- or alkyl-)phenyl); R^3 = R^1, benzoyl or benzoyl substituted with R^1 and R^2; there are < 5 Br atoms, < 4 F atoms, < 4 $COOR^7$ groups and > one $COOR^7$ group attached to any benzene ring), e.g., dibenzoyl resorcinol, effectively stabilise thermoplastic compositions, especially those made from vinyl or vinylidene halides, to prolonged exposure to light. C.O.C.

Protective Films having a Bright Reflective Metallic Lustre

Minnesota Mining & Manufacturing Co. *BP* 786,098

A protective and decorative film which adheres firmly to textiles, glass, metal, wood, etc. comprises a self-supporting transparent oriented polyester film > 2 mils thick, one side of which has been coated with a bright reflective metal film by vapour deposition in a vacuum. The polyester is a condensate of terephthalic and/or *iso*phthalic acid and ethylene glycol and/or other glycols. Coating of the polyester with metal is followed by application of an adhesive to the metallised surface. Effects resembling chrome plating are obtained by the use of such films which are flexible, tough and resistant to abrasion and weathering. C.O.C.

Monoazo Compounds as Absorbents for Ultraviolet Radiation (III p. 191)

Compositions containing Lead Chromate for Colouring Plastics (IV p. 202)

Lead Chrome Pigments for Colouring Cellulose Acetate (IV p. 202)

Iridescent Flake for use in Plastics (IV p. 202)

Inks for Printing on or Dyeing Plasticised Polyvinyl Acetal Sheeting (V p. 203)

Improving the Printability of Polyethylene Films (IX p. 210)

Artificial Fibre Sheeting as Paper Substitute (X p. 213)

Fibrillar Structure of Spherulites in Polyhexamethyleneadipamide (XIII this page)

XIV—ANALYSIS; TESTING; APPARATUS

Standards for pH Measurements from 60° to 95°C.

V. E. Bower and R. G. Bates

Bur. Stand. J. Res., **59**, 261–264 (Oct. 1957)

The National Bureau of Standards standard pH scale is now extended to the temp. range 60–95°c. E.M.F. measurements of cells with hydrogen and Ag–AgCl electrodes and containing buffer–KCl soln. are reported, and the derivation of pH_s (standard pH) values is described for the following five soln.— 0·05 m (molal) potassium tetraoxalate, potassium hydrogen tartrate (saturated at 25°c.), 0·05 m potassium hydrogen phthalate, 0·025 m potassium dihydrogen phosphate+0·025 m disodium hydrogen phosphate, and 0·01 m borax. Complete data from 0° to 95°c. are presented in tabular form and graphically. A.J.

Determination of Ethylene Oxide Condensates (Polyglycols) by Precipitation with Phosphotungstic Acid

H. Etienne

Parfums, Cosmét., Savons, (137), 33–37 (1957): *Chem. Abs.*, **51**, 17615 (25 Nov. 1957)

To a weighed sample (about 100 mg. of the detergent or the like being analysed) dissolved in 25 cc. CH_3OH, add 6 c.c. 6 N–HCl, 5 c.c. aq. 10% $BaCl_2{\cdot}2H_2O$ and (dropwise with stirring) 5 c.c. aq. 10% $P_2O_5{\cdot}24WO_3$. Dilute with 100 c.c. water, heat at 60°c. (water bath) by 10 min., cool for 18 hr. and filter. Wash the precipitate with 100 ml. water, dry for 8 hr. at 50°c. under 2–10 mm. mercury and then weigh. Wash 3–6 times with petroleum ether to remove fatty alcohols, redry for 2–3 hr. *in vacuo* at 50°c. and reweigh. Then ignite in a platinum crucible and reweigh. C.O.C.

Identification and Analysis of Natural Gums by Paper Chromatography and Electrophoresis

S. Marguier

Bull. Inst. Text. France, (67), 37–44 (May 1957)

The gum is hydrolysed with N-H_2SO_4, and the hydrolysate neutralised with $BaCO_3$ and concentrated. The resulting mixture of sugars is separated by paper electrophoresis using borate buffers or by paper chromatography using *n*-butanol–acetic acid–water (4:1:5 by vol.). The separated sugars are located by spraying with oxalic acid–aniline in acetic acid. The following examples of the use of the method are given— (*a*) absence of carob gum from a sizing preparation, (*b*) identification of alginate in a sizing preparation, (*c*) establishing identical nature of two gums used in printing formulations. J.C.F.

Rapid Amperometric Determination of Starch

J. Holló and J. Szejtli

Élelmezési Ipar., **10**, (4), 98–100 (1956): *Hungarian Tech. Abs.*, **9**, (2), 55 (1957)

The volumetric method is based on the principle that plain platinum electrodes are polarised if a potential is applied, and that they will depolarise— if iodine is introduced into the system— to a degree corresponding to the concentration of the iodine present. The current flowing through the system is proportional to the concentration of the free iodine, which in turn depends on the amylose content of the solution. The end-point of the titration is indicated by the galvanometer deflection: no free iodine is present at the end-point, and consequently no current flows through the solution. If amylose or starch is titrated, free iodine is present near the end-point in amounts corresponding to the equilibrium concentration, and by measuring the current at this point the concentration of free iodine present may be calculated. Advantages of the method are— rapidity (a determination takes about 25 min.), a minimum of chemicals required, reliable results (within an average analytical error of 1%), reducing carbohydrates and dextrins present do not interfere, and finally adaptability to automatic titrations. The drawback of the method is that it measures amylose only and not the starch, but the amylose content may generally be considered as a relatively stable value. Oxidising agents and substances which react with iodine interfere with the determination. C.J.W.H.

Fast Sulphur Black F (C.I. 26990) as an Indicator for the Titration of Copper with Ethylenediaminetetra-acetic Acid

R. Belcher, R. A. Close, and T. S. Wert

Chem. and Ind., 1647 (21 Dec. 1957)

The title dye is virtually specific in its colour reaction with cupric copper, which, in the presence of ammonia, is crimson with cupric ions, changing back to green with excess of ethylenediaminetetra-acetic acid. In moderately strong soln. the blue colour of the cuprammonium ion causes the colour change to be from pale blue to bright green. With a large amount of indicator, the red-to-green end-point occurs too soon and is less distinct. Nickel is the only other ion of many examined which forms a coloured product, but the nickel complex cannot be used satisfactorily as an indicator. The presence of ammonia is essential for colour formation, which suggests that the constitution of the complex is such that two ammonium mol. are probably co-ordinated with the copper atom. Pyridine, which also gives a red colour, reacts too sluggishly for use in place of ammonia. H.H.H.

Complexometric Determination of Iron in the presence of Variamine Blue (C.I. Azoic Diazo Components 22, 35, and 47) Indicator

L. Erdey and G. Rády

Magyar Tudományos Akadémia Kémiai Tudományok Osztályának Közleményei, **8**, (1), 67–75 (1956): *Hungarian Tech. Abs.*, **9**, (3), 76 (1957)

Iron(III) ions can be titrated at room temperature with standard complexon III (ethylenediaminetetra-acetic acid) solution in the presence of Variamine Blue indicator at pH 1·7–2·8; with 0·1 and 0·01 M. concn. the relative error is ±0·112%, and standard deviations do not exceed ±0·104 ml. However, ions of several metals (such as copper, bismuth, cobalt, cadmium, aluminium, zinc) interfere with the titration. The main reaction is considerably delayed by the presence of fluoride and phosphate. Nitrate does not interfere. Moreover, it was found that complexon III solutions can be titrated well with standard iron(III) solutions at about 50°c. and at pH 3·0–4·5. C.J.W.H.

Photometric Determination of Thallium with Rhodamine B (C.I. Basic Violet 10)

H. Onishi

Bull. Chem. Soc. Japan, **30**, 567–571 (Sept. 1957)

Chromatography of Dye Intermediates. VII—Identification of Toluidines and Nitrotoluenes by Paper Chromatography

J. Latinák

Chem. Listy, **51**, 1493–6 (1957): *Chem. Abs.*, **51**, 16208 (20 Nov. 1957)

Br derivatives obtained by titrating ice-cooled solution of isomeric toluidine in dil. HCl with 0·1 M $_3KBrO_3$ containing KBr was extracted with benzene and separated by descending chromatography. Whatman No. 4 paper impregnated with 10% benzene solution of paraffin in ethanol–water–acetic acid (20:14:1) was used, and detection was made with a freshly prepared 0·5% solution of 2-naphthol-3:6-disulphuric acid in 5% aq. Na_2CO_3. Nitrotoluenes were similarly identified after valuation with Zn powder in HCl. Sensitivity is 0·3–0·5 *v*. Ring-substituted derivatives have the advantages of lowered volatility and improved chromatographic separation. R_f values are given for 2:4:5-tribromoaniline 0·23, 2:4:6-tribromo-*m*-toluidine 0·13, 2:6-dibromo-*p*-toluidine 0·28, and 4:6-dibromo-*o*-toluidine 0·50. C.O.C.

Reversed-phase Chromatography. I—Identification of Solvent Dyes

M. R. Verma and R. Dass

J. Sci. Ind. Research (India), **16B**, 131–4 (1957): *Chem. Abs.*, **51**, 15817 (25 Oct. 1957)

Solvent dyes were distinguished from one another by suitable choice of impregnated filter paper and eluant. R_f values of 22 dyes are given as well as their C.I. numbers and status as food dyes. C.O.C.

Reverse-phase Chromatography in the Analysis of Solvent Dyes

M. R. Verma and R. Dass

Naturwissenschaften, **44**, 351 (1957): *Chem. Abs.*, **51**, 17613 (25 Nov. 1957)

Filter papers (Whatman No. 1, 18 in. × 12 in.) were rendered water-repellent by (1) acetylation, or (2) Dow-Corning Silicone 1107, or (3) paraffin, or (4) oleic acid. The dyespots were fed on the base-line and developed with an aqueous solution of various solvents by the ascending method. Several eluant systems were investigated for each of the modified papers and in some of these very clear resolution could be obtained. The technique was used to

identify some commercial dyes by comparing the R_f values of unknown dyes with those of known dyes. C.O.C.

Extraction and Identification of Synthetic Dyes in Foods— I
R. De Gori and P. Cantagalli
Boll. lab. chim. provinciali (Bologna), **8**, 23–6 (1957): *Chem. Abs.*, **51**, 18361 (25 Nov. 1957)

Naphthol Yellow S (I), Tartrazine (II) and Chrysoidine (III) are separated by ascending chromatography on Whatman No. 1 paper using as solvent ethanol (1), water (1), butanol (2), and ammonia (d. 0·910) (1). The R_f values are I— 0·35, II— 0·05, and III— 0·89. After separation, the spots can be cut out and eluted for spectrophotometric determination. I and II are eluted with distilled water, and III with alcohol. Absorption curves for the three dyes are given. C.O.C.

Chromatography of Synthetic Colours in Pharmaceutical Preparations for Internal Use
J. M. P. Delfina and R. S. Marcián
Galénica Acta (Madrid), **9**, 243–286 (1956): *Chem. Abs.*, **51**, 17104 (20 Nov. 1957)

The preparations (10 g.) were extracted with water at 60°c. The insoluble portion (I) was re-extracted with 5% tartaric acid at 60–80°c., dyed on wool, eluted with 0·02 N NH_3, concentrated, and developed on Schleicher & Schull 2043A paper with water-saturated butanol or $(ClCH_2)_2CHOOH$. Thus were determined: C.I. Food Yellow 3, C.I. Acid Yellow 3, 9, and 23, C.I. Vat Blue 4, C.I. Acid Blue 74, C.I. Acid Red 13, 14, 18, 27, 44, and 73. The soluble fraction was divided into liquid A (II) and B (III). II was acidified with 5% tartaric acid, dyed on wool and eluted as above, and extracted with ammonia. The aqueous phase contained the same dyes as I. The alcoholic phase contained Brilliant Blue B, C.I. Acid Blue 83, C.I. Acid Red 73 and 88, and C.I. Pigment Red 163, C.I. Acid Violet 17 and 49. III was treated with 5% NaCl and the dyes transferred to wool, eluted with *N*-tartaric acid and extracted with chloroform. The extract contained C.I. Basic Yellow 2, C.I. Basic Blue 11 and 26, C.I. Basic Violet 1, 10 and 14 and C.I. Basic Green 1. Photographs of paper chromatograms are given with details of the experiments. C.O.C.

Determination of Quercetin (C.I. 75670) and Rutin (C.I. 75730)
D. G. Constantinesco and R. Oteleanu
Acta Polon. Pharm., **14**, 27–32 (1957): *Chem. Abs.*, **51**, 15889 (25 Oct. 1957)

These two dyes form yellow complexes with $SbCl_3$. The quercetin complex shows no light absorption between 470–500 mμ, whereas the rutin complex does. In photometric determination of quercetin and rutin in their mixtures, quercetin is determined directly from the extinction at 470 mμ of its $SbCl_3$ complex in methanol. A separate sample is then hydrolysed with 1% HCl in methanol, neutralised with Na_2CO_3 and the total quercetin (original and that from hydrolysed rutin) is similarly determined. The difference between the two measurements gives the amount of rutin present. C.O.C.

Determination of Carotene (C.I. 75130) in Foods
A. Inczédy and E. Demel
Elelmezési Ipar., **10**, (7), 221–225 (1956): *Hungarian Tech. Abs.*, **9**, (3), 78 (1957)

A weighed sample is pounded with quartz sand in a mortar, and then washed into a flask with alcoholic KOH; after addition of petroleum ether, the mixture is refluxed for 30 min. The substance is cooled, and the KOH layer separated into a funnel and diluted with water; then NaCl is added, and the material washed with petroleum ether until the solvent remains colourless. The combined petroleum ether solutions are washed with water to remove alkalinity, dried with anhydrous sodium sulphate, and concentrated to 2–3 ml.vol. under reduced pressure. This concentrated solution is adsorbed on a chromatography column of freshly prepared calcium hydroxide with a suction of 300 mm. When the α- and β-carotene bands have separated, the column is pushed out of the chromatography tube, and the carotene rings are cut out, placed in a beaker, moistened with ethanol, transferred to a sintered-glass filter, and washed with petroleum ether until the colour disappears. The alcohol is washed from the mixture with water in a separating funnel, and the petroleum ether solution is dried over sodium sulphate and analysed in a Pulfrich photometer with an S 47 filter. By comparing the various methods it has been established that only the procedure described yields reliable results in the assay of carotene in foodstuffs. C.J.W.H.

Crystallisation of Organic Pigments
G. Bleisch
Farbe u. Lack, **63**, 341 (1957): *Chem. Abs.*, **51**, 15965 (25 Oct. 1957)

Careful crystallisation of organic pigments from dilute $CHCl_3$ solution will often yield readily identifiable crystals. Examples of several pigment crystals are shown in coloured photomicrographs. C.O.C.

Determination of the Specific Surface of Leafing Aluminium Flake Pigments (C.I. Pigment Metal 1) in Pastes
T. Rehner and L. Klimits
Farbe u. Lack, **62**, 464–8 (1956): *Chem. Abs.*, **51**, 17195 (20 Nov. 1957)

An accurate method is to wash off the leafing agent with a petroleum solvent (b.p. 60–90°c.), dry and powder the dry pigment with a spatula, violently disperse a weighed amount in water by a magnetic stirrer and transfer the pigment quantitatively to the measuring trough. Use of a petroleum solvent instead of acetone or petroleum ether minimises the tendency of the washed pigment to become lyophilic and thus not spread properly in the measuring trough. C.O.C.

Differentiation of Titanium Dioxides
W. Lamprecht
Farbe u. Lack, **63**, 342–5 (1957): *Chem. Abs.*, **51**, 15965 (25 Nov. 1957)

Rutile and anatase are best distinguished by X-ray diffraction. Other physical measurements are unreliable because of small differences in physical properties between the two forms of the oxide. A simple iodometric method based on the difference in photochemical activity of anatase and rutile is proposed. C.O.C.

Determination of the Transparency of Printing Inks especially with respect to the Validity of Lambert's Law
A. Karsai
Papír-és Nyomdatechnika, **8**, (4), 98–102 (1956): *Hungarian Tech. Abs.*, **9**, (2), 57 (1957)

The optical properties of the coloured film formed by printing ink are investigated. The path of monochromatic light rays is influenced by a number of factors, such as the varnish, the kind of pigment, the shape of the pigment, the independent optical properties of the aluminium hydroxide, the paper, and the mutual effects of all these. With certain simplifications it was deduced that the logarithms of the curves of density of a colour film are parallel for various thicknesses, and that the displacement is the logarithm of the film thickness referred to the unit. Density and relative thickness are viewed on colour films applied to glass plates. By plotting the logarithm of relative thickness as a function of the logarithm of density, a straight line inclined at 45° is obtained if the above relationship is valid, this line intersecting the ordinates axis at unit thickness. Deviations between the measured and calculated values are 8–10%. C.J.W.H.

Textile Users of Nuclear Radiation
AATCC Committee on Nuclear Radiation
Amer. Dyestuff Rep., **46**, P 777–P 778 and P 780 (21 Oct. 1957)

This review of the uses of nuclear radiation in the textile industry is compiled from a list of those people licensed by the U.S. Atomic Energy Commission to use radioactive substances. Strontium 90 is used to measure the thickness of rubber and resin coating on fabrics. Dye uptake and fastness to washing, abrasion, etc. can be measured using a radioactively "tagged" dye. The absorption of radioactive ions by hair has been studied. Detergent problems including detergent absorption by fibres and soiling tests, the biosynthesis of cellulose, and the movement of fibres in spinning and drafting are all amenable to this method of investigation. Cellulose degradation and polymerisation initiation by radiation are also mentioned. P.T.S.

Textile Flexometer
Z. Weisz

Tint. ind., (30), 373–377 (Aug. 1957)

Reference is made to a Russian method for measuring the recovery from creasing of accordeon-pleated patterns and to the Honigmann apparatus, in which a creased circular pattern is revolved on a gramophone turntable and the raised portions mapped by a spiralling electronic contact. Since in wool, creases are not angular but in the shape of arcs, the Flexometer forms a loop of fabric (20 mm. wide, 80 mm. long, and 15–20 mm. high), the ends of which are gripped between jaws. The patterns are cut on the bias at various angles to the warp and weft and loaded with 3 kg. for 3 min. The widths of the loop before and after loading (a' and a'') are measured by projecting the silhouette, when the creasing coefficient is given by—

$$K = \frac{a' - a''}{a'} \times 100\%$$

S.R.C.

Rapid Determination of the Moisture Content of Textiles by a Modified Marcusson Apparatus
T. Asbóth and B. Mihalik

Magyar Textiltechnika, (2), 57–60 (1956):
Hungarian Tech. Abs., **9**, (1), 20 (1957)

Several hundreds of measurements were carried out on different textiles and textile raw materials with the modified Marcusson apparatus. The samples to be investigated were placed in a sealed container for several days, and then their moisture content was simultaneously determined by conditioning and by the modified Marcusson apparatus. The results proved the accuracy of the moisture determinations in the Marcusson apparatus to be 0·5% and the mean deviation to be smaller than with the method used thus far. With the new type of apparatus all the water can be distilled from the sample since the water cannot return into the flask. The apparatus is small, and therefore requires little space, and the process is considerably faster and more economical than conditioning.

C.J.W.H.

Moisture Content of Textile Fibres with the Karl Fischer Reagent
F. Péter

Magyar Textiltechnika, (8), 274–277 (1956):
Hungarian Tech. Abs., **9**, (3), 90 (1957)

Conditioning, the most commonly used industrial method for testing the moisture content of fibrous materials, has many disadvantages. It requires large quantities of testing materials, consumes a great deal of time, and is not sufficiently precise. When testing the moisture content with the well known Karl Fischer reagent, the extraction of moisture and the titration must be carried out separately. Special retorts were made for the purpose, thereby improving the precision of the Karl Fischer method. Since this method is cheaper and quicker than conditioning, it is recommended for industrial use.

C.J.W.H.

Cotton Fibre Maturity Test—Estimation by Classification of Fibres swollen in Caustic Soda Solution
Textile Institute

Tentative Textile Standard, No. 47 (1957):
J. Textile Inst., **48**, P 777–P 781 (Dec. 1957)

"Cotton fibre maturity" is related to the extent of fibre wall development. For cottons of similar length and perimeter, mature cottons with thick walls usually give fewer neps, are more lustrous, and dye deeper colours than immature cottons with thin walls. Fibre maturity is related to the ratio of the cross-sectional area of the fibre wall to the area of a circle with the same perimeter as the fibre. Fibres are swollen in $18 \pm 0{\cdot}2\%$ caustic soda, examined under the microscope, and put into three categories— normal, thin-walled, or dead fibres. The maturity M is given by the empirical formula—

$$M = \frac{N - D}{200} + 0{\cdot}70$$

where N is the percentage of normal fibres, and D the percentage of dead fibres.

P.T.S.

Quantitative Chemical Analysis of Mixtures of Viscose Rayon and Cotton
Textile Institute

Tentative Textile Standard, No. 49 (1957):
J. Textile Inst., **48**, P 784–P 786 (Dec. 1957)

The viscose rayon is dissolved at room temperature from a known dry weight of the mixture by means of a sodium zincate solution (method of preparation given). The residue of cotton is collected, washed, dried, and weighed. The weight is corrected for the amount lost in the sodium zincate (unscoured 4%; scoured, kiered, or bleached 2%), and expressed as a percentage of the weight of the mixture.

P.T.S.

Rapid Method for detecting Viscose Rayon Yarns mixed with Cotton Warp Yarns
M. Országh

Magyar Textiltechnika, (8), 311 (1956):
Hungarian Tech. Abs., **9**, (3), 90 (1957)

The presence of viscose rayon among cotton warp yarns can be detected within a few minutes on the loom itself by the adequate use of a mildly acid or neutral chromium-complex dye. The grey cloth on the loom should be rubbed lightly, e.g. with a cold 25% solution of Irgalan Grey BL (C.I. Acid Black 58). The highly hydrophilic viscose rayon yarns instantly absorb the aqueous dye solution, whereas the hydrophobic cotton yarns remain grey. Thus the presence and the location of the alien viscose rayon yarn may be detected.

C.J.W.H.

Determination of Viscose Rayon and Cotton in Blend Yarns and Fabrics using Sodium Zincate Solution
W. Armfield

J. Textile Inst., **48**, T 503–T 505 (Dec. 1957)

Sodium zincate (details of preparation given) can be used without ammonium thiocyanate to dissolve viscose rayon from mixtures with raw, scoured, or bleached cotton. Unlike previous methods, this one does not require careful temperature control: room temp. between 15° and 25°c. is satisfactory. Cotton is not completely insoluble in sodium zincate, and a correction factor has to be applied which depends on whether the cotton has been scoured or bleached. The percentage cotton found is multiplied by 1·04 if unscoured, 1·02 if it is scoured, kiered, or bleached. The test is not recommended if the cotton has a cuprammonium fluidity greater than 14.

P.T.S.

Quantitative Chemical Analysis of Binary Mixtures of Polyamide Fibres and certain other Fibres
Textile Institute

Tentative Textile Standard, No. 48 (1957):
J. Textile Inst., **48**, P 782–P 783 (Dec. 1957)

Polyamide fibres are removed from the mixtures by dissolving them in 80% formic acid. The residue is collected, washed, dried, and weighed. Its weight is corrected where necessary for loss in formic acid, and expressed as a percentage of the weight of the mixture.

P.T.S.

Development of Detergents for Raw Wool Scouring
F. F. Kobayashi

Amer. Dyestuff Rep., **46**, 694–695 (23 Sept. 1957)

This paper describes the testing of three neutral synthetic detergents (not specified) for raw-wool scouring in a miniature scouring train and a pilot scouring train at the Lowell Technological Institute, Lowell, Mass., U.S.A.

P.T.S.

Micro Dyeing Apparatus for Laboratory Use
F. Péter and B. Mihalik

Magyar Textiltechnika, (5), 163–164 (1956):
Hungarian Tech. Abs., **9**, (2), 57 (1957)

The motion of the sample to be dyed and evaporation of the dyeing liquor make evaluation of the dyeing experiments conducted in the customary laboratory equipment rather uncertain. This is obviated by use of the new dyeing apparatus, which is made entirely of glass; it may be placed in a thermostatically controlled water-bath, or if necessary directly heated. The dimensions of the dyeing chamber are small, since it is used for the dyeing of small samples only. The liquor ratio is variable within wide limits, and the dyeing processes are visible to the naked eye. Vat and sulphur dyes can be studied especially well in the new micro apparatus. It is simple to operate, production costs are relatively low, and it is suitable for use in research laboratories and for educational purposes.

C.J.W.H.

Microdesorption Method for Determining the Adsorption Equilibrium and Heat of Dyeing
A. Yabe and A. Uchida

Yûki Gôsei Kagaku Kyôkaisha, **13**, 601–4 (1955):
Chem. Abs., **51**, 17307 (25 Nov. 1957)

200–400 mg. of wool slubbing (previously thoroughly washed in 0·5 g./l. Lissapol N at 40–50°c. for 30 min., then

dyed for 2 hr. at 95°c. with 5% Orange II (C.I. Acid Orange 7), 3% H_2SO_4 and 10% Na_2SO_4) was packed into a bulb formed by the bottom of one of two tubes connected with a capillary tube to form a U-shaped microdesorption cell. The wool was then desorbed by circulating a similar liquor containing no dye to and from the other tube at 60°c. for 25 min., followed by three periods of 5 min. each, each time using a fresh liquor. The dye desorbed into the liquors was determined. From this the adsorption equilibrium was calculated to be 95·70 – 6·32% and the heat of dyeing – 13·8 Kcal./mole. C.O.C.

Analysis of Used Fur-dyeing Baths containing Oxidation Dyes

F. Brugger and L. Párizs

Bőr-és Cipőtechnika, **6**, (2), 38–39 (1956): *Hungarian Tech. Abs.*, **9**, (2), 54 (1957)

The percentage of solids and the ash content are not characteristic of the degree of exhaustion of the dyebath. The *p*-phenylenediamine content of the bath cannot be determined by direct kjeldahlometry, since the measurement will yield low values for nitrogen. In order to obtain reproducible results, the solution should be reduced with Zn and dil. H_2SO_4 before the wet-combustion stage. The phenol content of the bath was determined by the Koppeschaar method after a preliminary separation by steam distillation. The hydrogen peroxide content was measured volumetrically by titrating the iodine solution obtained by chloroform extraction of the iodine liberated after acidification and addition of K.I. It was found that the results were about 2% lower if *p*-phenylenediamine was present. The dyebaths examined contained 0·2–0·4 g. *p*-phenylenediamine, 0·5–0·6 g. phenol, and 0·12–0·16 g. hydrogen peroxide per litre after use. C.J.W.H.

Variables encountered in Natural Light Fading

AATCC Committee on Colour Fastness to Light

Amer. Dyestuff Rep., **46**, P 861–P 883 (18 Nov. 1957)

Six dyeings on nylon, six on wool, six on cotton, six on viscose rayon, and four commercial automotive fabrics, all of which had given variable results in colour fastness tests, were used in the work described here. Sunlight is too variable to give satisfactory, reproducible results, whether the test piece is exposed for 24 hr. a day or only between 9 a.m. and 3 p.m. The most important factor in fading is the total amount of radiation expressed in langley units— gram-calories per square centimetre per minute— and the degree of fading for a specified number of langley units is a good measure of light fastness. Other factors, however, are involved— temperature of the specimen, its moisture content, and the intensity and spectral distribution of the radiation. There is, however, no threshold of radiation intensity below which fading cannot occur. P.T.S.

Determination of Colour Fastness to Light

M. L. Staples

Canadian Textile J., **74**, 81–85 (28 June 1957)

Recent Investigations in the U.S.A. on Sun, Daylight Test Methods

C. H. A. Schmitt

Canadian Textile J., **74**, 57–65 (23 Aug. 1957)

Observations at a number of stations in the U.S.A. show that sunlight tests do not give reproducible results when the exposures are for equal numbers of sun-hours, i.e. the times for solar radiation above 0·223 g.cal./cm.²/min. Exposures for the same total solar radiation, measured in langley units, give much better reproducibility at different locations, but some anomalies, particularly on cotton and nylon, may occur under extremes of humidity and temp. A.J.

Colour Fastness to Light Testing in the Fade-Ometer

J. E. Norton

Canadian Textile J., **74**, 45–50 (26 July 1957)

A description of the Model FDA–R Fade-Ometer and its use. Particular attention is given to the importance of the correct black-panel temperature of the specimens and the means of ensuring this. A.J.

Two New Dry-cleaning Test Methods

AATCC Committee on Dry-cleaning Test Methods

Amer. Dyestuff Rep., **46**, P 859–P 860 and P 884 (18 Nov. 1957)

(i) Colour Fastness to Dry Cleaning— Tentative Test Method 85–1957. A specimen is agitated in perchlorethylene containing a dry-cleaning soap and steel balls to simulate the mechanical action in dry cleaning. The fading of colour is estimated by reference to the International Geometric Grey Scale.

(ii) Durability of Applied Designs and Finishes to Dry Cleaning— Tentative Test Method 86–1957. The same method is used in three tests— one with perchlorethylene and soap, one with white spirit, and a third with perchlorethylene but without soap. A large specimen can be used to reproduce commercial conditions. The effects on applied designs and handle are estimated visually and manually, respectively. The effect on applied finishes is determined using the standard AATCC test methods. P.T.S.

Colour Fastness to Solvent Crocking

C. Teichgraber

Canadian Textile J., **74**, 55–57 (12 July 1957)

The test is sponsored by the Canadian Government Specifications Board, for the purpose of evaluating the performance of dyed and printed textiles on dry-cleaning and spot cleaning. The test fabric is rubbed 10 times in each direction with a white fabric, both being thoroughly wetted with perchlorethylene, using a device such as the AATCC crockmeter. Defects are apparent as— (*a*) ring formation, due to migration of dye or finish; (*b*) whitening of fabric surface, due to poor adhesion of dye; (*c*) transfer of colour to undyed material. Vat, azoic, and disperse dyes appear to be the most commonly affected, particularly the last-named when present in deep colours on hydrophobic fibres. W.K.R.

Formaldehyde Evolution from Textiles

O. C. Bacon, M. F. Parker, and L. F. Horn

Amer. Dyestuff Rep., **46**, P 933–P 936 (2 Dec. 1957)

Eight test methods are considered for the estimation of formaldehyde evolved from resin-treated fabrics. In the method chosen the fabric is sealed in a jar containing also a glycerol–water mixture of known relative humidity. The temperature of the experiment is controlled. The amount of formaldehyde absorbed by the glycerol–water is estimated photometrically using a colour reaction of formaldehyde with phenylhydrazine, potassium ferricyanide, and sodium hydroxide. A low ratio of formaldehyde to dimethylolethyleneurea in the original treatment lowers the subsequent formaldehyde evolution; a neutralising wash after treatment, and the use of magnesium chloride instead of an amine hydrochloride as catalyst in the treatment, both lower formaldehyde evolution later. The paper contains a curve showing the variation of R.H. with the composition of the glycerol–water mixture at 25° and 60°c. P.T.S.

Silicone Resins in Finishing

M. Carru

Teintex, **22**, 924–949 (Dec. 1957)

The various finishes and processes are reviewed. A silicone finish may be detected by ashing, mixing with ammonium fluoride and conc. H_2SO_4, and gently warming, all in Pt. White vapours of SiF_4 are evolved, giving a film of SiO_2 on a drop of water. If CH_3COONa solution is used in place of water, microscopic crystals of silicofluoride are formed. Ammonium molybdate paper turns yellow in the white vapours, the silicomolybdate being also formed if treated fabric or liquid containing silicones is heated with ammonium molybdate solution to 100°c. For quantitative determination a Kjeldahl estimation, followed by addition of distilled water, filtering, and ashing of the SiO_2 precipitate, is recommended.

The influence of the following factors on a silicone proof is considered— dosage of silicone, time and temperature of polymerisation, nature and ratio of catalyst, pH of fabric, and quality of desizing before treatment, life of impregnating liquor, inorganic salts, and number of baking treatments. S.R.C.

Optical Properties of some Dyes in a "Massive" State by the Mirror Reflection Method (IV p. 193)

Bleed Resistance of Printing Ink Pigments (V p. 203)

New Method of Examining Fibre Cross-sections by Electron Microscopy— Application to the Structure of Wool (VI p. 205)

Rapid Method of Fractionation of Viscose Rayon and Cellulose of Low Degree of Polymerisation (XI p. 214)

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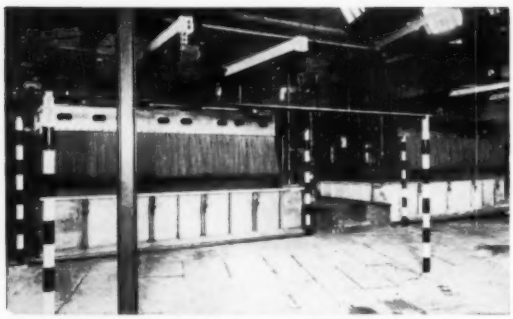

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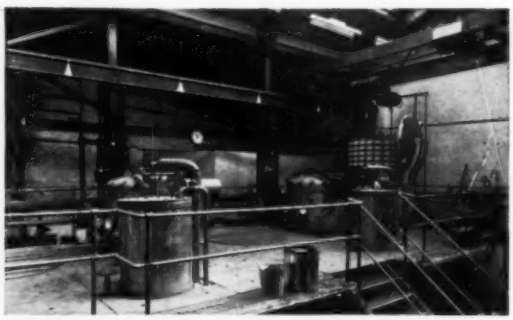
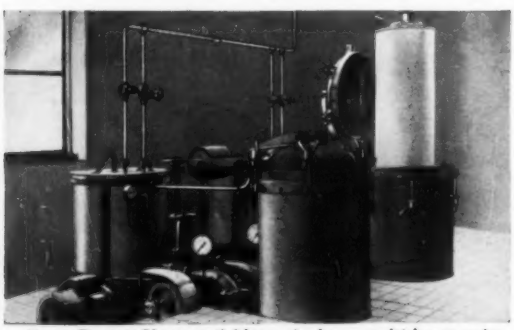


Installation of Pressure Dyeing Plant for fast colours on cotton cheeses, cones and hanks



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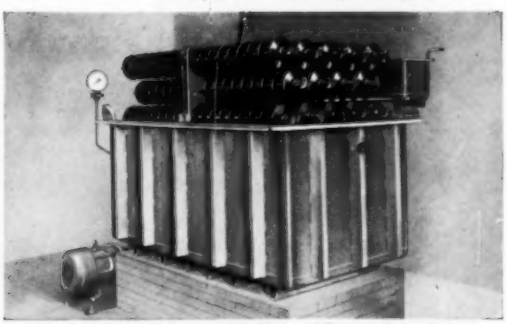

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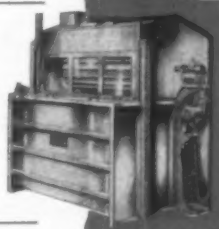

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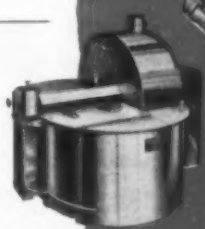

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